

# RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXI

NUMBER 1



January, 1948

123  

---

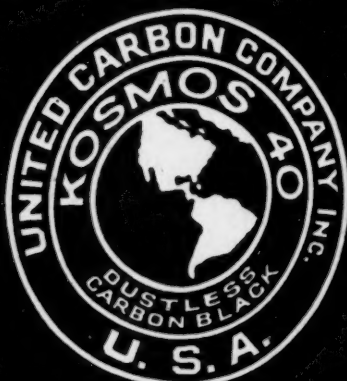
*Published Quarterly under the Auspices of the*  
DIVISION OF RUBBER CHEMISTRY  
*of the*  
AMERICAN CHEMICAL SOCIETY  
*at Prince and Lemon Sts., Lancaster, Pa.*

---

NET WEIGHT 50 LBS.

KOSMOS 40

KOSMOS 40



KOSMOS 40

KOSMOS 40

MADE IN U.S.A.  
PATENTS APPLIED FOR

The furnace-process reinforcing carbon black (HMF type) for synthetic and natural rubber. Easy processing; smooth and rapid extrusion; full reinforcement; low heat build-up; high resiliency; high resistance to cut growth, flex cracking and abrasion. Excellent for blending with channel black in GR-S tread stock to secure better plasticity.

**UNITED CARBON COMPANY, INC.**

CHARLESTON, WEST VIRGINIA

New York — Akron — Chicago



# RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XXI

NUMBER 1



January, 1948

---

*Published under the Auspices of the*  
DIVISION OF RUBBER CHEMISTRY  
*of the*  
AMERICAN CHEMICAL SOCIETY

---

# CARBON BLACKS

*for* RUBBER COMPOUNDING

•  
MPC (Medium Processing Channel)  
**STANDARD MICRONEX**

•  
EPC (Easy Processing Channel)  
**MICRONEX W-6**

•  
HMF (High Modulus Furnace)  
**STATEX-93**

•  
FF (Fine Furnace)  
**STATEX-B**

•  
VFF (Very Fine Furnace)  
**STATEX-K**

•  
FEF (Fast Extruding Furnace)  
**STATEX-M**

•  
SRF (Semi-Reinforcing Furnace)  
**FURNEX**

• COLUMBIAN COLLOIDS •

COLUMBIAN CARBON CO. • BINNEY & SMITH CO.  
MANUFACTURER DISTRIBUTOR



400 TONS OF SMOKE A DAY

# RUBBER CHEMISTRY AND TECHNOLOGY

Published quarterly under the Auspices of the Division of Rubber Chemistry  
of the American Chemical Society,  
Prince and Lemon Streets,  
Lancaster, Pa.

Editor.....C. C. DAVIS  
Advertising Manager.....S. G. BYAM  
Secretary.....C. R. HAYNES  
Treasurer.....C. W. CHRISTENSEN

Vol. XXI

January, 1948

No. 1

## CONTENTS

### General Section

	PAGE
Officers.....	iii
Spring Meeting of the Division of Rubber Chemistry of the American Chemical Society, Cleveland, Ohio, May 26-28, 1947.....	vii
Fall Meeting of the Division of Rubber Chemistry of the American Chemical Society, New York, N. Y., September 17-19, 1947.....	ix
New Books and Other Publications.....	xi

### Reprinted Papers

Vulcanization of Rubber With Sulfur. IRA WILLIAMS.....	1
Sulfur Linkage in Vulcanized Rubber. Reaction of Sulfur With 2-Methyl-2-Butene. MILTON L. SELKER AND A. R. KEMP.....	14
Certain Fundamental Concepts Relating to Nonpolar Mechanisms in Olefinic Systems. E. H. FARMER.....	27
The Addition of Thiocompounds to Olefins. I. Reactions of Thioglycolic Acid, Thiophenol, and Isopentanethiol. J. I. CUNNEEN.....	41
Structural Changes in Rubbers Brought About by Molecular Oxygen. B. DOGADKIN.....	47
The Action of Benzoyl Peroxide on Natural Rubber in Solution. PATRICE COMPAGNON AND ANDRÉ DELALANDE.....	60
Influence of Structure on Polymer Liquid Interaction. I. Relative and Absolute Values of Swelling Equilibria. G. SALOMON AND G. J. VAN AMERONGEN.....	66
Heat Conduction and Molecular Structure in Rubberlike Polymers. JOHN REHNER, JR.....	82
Low Temperature Characteristics of Elastomers. S. D. GEHMAN, D. E. WOODFORD, AND C. S. WILKINSON, JR.....	94
Variation in the Specific Heat of Rubber as a Function of Elongation. ANDRÉ MAYOR.....	112
Rubberlike Products From Linear Polyesters. B. S. BIGGS, R. H. ERICKSON, AND C. S. FULLER.....	115
The Solubility of Gases in Elastomers. R. M. BARRER.....	133
A Radiographic Study of Rubber-Sulfur Mixtures. J. J. TRILLAT.....	141
Plasticization of Natural and Synthetic Rubbers. I. G. H. PIPER AND J. R. SCOTT.....	149
Statistical Analysis of Plasticity Measurements of Natural and Synthetic Rubber. M. C. THRODAHL.....	164
Method of Testing the Mechanical Properties of Vulcanizates Prepared From Latex as a Starting Material. MARCEL PIROT.....	168

Oven and Bomb Aging of GR-S at Corresponding Temperatures. J. REID SHELTON AND HUGH WINN.....	180
Methods of Averaging Physical Test Results. Use of Median. J. M. BUIST AND O. L. DAVIES.....	188
Chromatographic Analysis of Rubber Compounding Ingredients and Their Identification in Vulcanizates. L. J. BELLAMY, J. H. LAWRIE, AND E. W. S. PRESS..	195
Device for Evaluating Surface Cracking of Gr-S. M. C. THRODAHL.....	220
Crude Rubber Preparation. Sheet Production by Continuous Coagulation of Hevea Latex. E. B. NEWTON, W. D. STEWART, AND E. A. WILLSON.....	226
Chemical Changes in Ammoniated Hevea Latex. R. F. A. ALTMAN.....	241
The Thermoplasticity of Thermoprene. A Study of the Adhesion of Rubber to Metal. ANDRÉ JARRIJON AND PIERRE LOUÏA.....	247
Determination of Resistance to Abrasive Wear. V. Influence of Calendar Grain. R. W. PARRIS AND J. R. SCOTT.....	254
VII. Uniformity of Results Obtained With the Du Pont Machine. J. F. MORLEY AND J. R. SCOTT.....	257
Hardness Testing of Vulcanized Rubber. V. Investigation of the Ball Indentation Test. Part 3. Condition of The Rubber Surface. E. H. DOCK AND J. R. SCOTT	262
The Effect of Air Circulation by Convection in the Test-Tube Method of High-Temperature Aging of Synthetic Rubbers. A. E. JUVE, H. BOXSER, D. H. REAHARD, JR., S. R. DONER, J. F. MCWHORTER, C. G. CASHION, G. D. MCCARTHY, AND R. M. HOWLETT.....	271
Effect of Fungicides on Natural and Synthetic Rubber. J. L. STIEF, JR., AND J. J. BOYLE.....	276

## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues (\$2.50 per year) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Anyone who is not a member of the American Chemical Society may become an Associate Member of the Division of Rubber Chemistry upon payment of \$5.00 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at the subscription price of \$5.00 per year.

To these charges of \$2.50 and \$5.00, respectively, per year, postage of \$.20 per year must be added for subscribers in Canada, and \$.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio.

Articles, including translations and their illustrations, may be reprinted if due credit is given RUBBER CHEMISTRY AND TECHNOLOGY.

# VULCANIZATION OF RUBBER WITH SULFUR \*

IRA WILLIAMS

J. M. HUBER CORPORATION, BORGER, TEX.

Vulcanization is a change in rubber which results in an increased resistance to deformation at ordinary temperature. This definition disregards entirely any chemical agents or chemical actions involved. It requires only that the rubber lose its plastic properties and become more resistant to compression, stretching, or swelling. Freeze resistance may or may not be affected; this depends largely on the extent of any chemical attack which may be involved.

The earliest method of vulcanization, discovered by Goodyear over a hundred years ago, still remains the basis for essentially all vulcanization of rubber today. The only refinements which have been introduced consist in the addition of accelerators and accelerating accessories, and in a manipulation of the quantity of sulfur. All of the other methods, such as the use of sulfur chloride, peroxides, quinones, nitro compounds, and selenium, remain quite unimportant from a commercial standpoint.

The study of vulcanization, particularly with sulfur, has received the attention of many chemists, most of whom have differed in their final interpretation of the action. The earliest work on the nature of vulcanization was carried out by Henriques<sup>1</sup>, who found that sulfur chloride combines chemically with rubber, and the natural assumption was made that molecules of rubber are joined by means of sulfur. Weber<sup>2</sup> soon found that sulfur combined during hot vulcanization. Stern<sup>3</sup> found that the amount of sulfur combined was directly proportional to the time of heating and depended on the original concentration of sulfur. Whereas Stern conducted his vulcanization in solution, Hübener<sup>4</sup> obtained substantially the same results in a direct manner.

Many theories have been evolved to explain the mechanism of vulcanization. Höhn<sup>5</sup> and particularly Ostwald<sup>6</sup> believed it to be an adsorption phenomenon. This was soon disproved. The majority of investigators at present are inclined to favor some sort of chemical reaction which produces bonding of some type between molecules, either from cross-linking, by means of sulfur, by polymerization, or by molecular association. All of these theories recognize that in some manner the combination of sulfur is instrumental in the process.

Considerable work<sup>7</sup> has been done on combining sulfur with relatively simple organic molecules in attempts to gain some information regarding the manner of addition of rubber and sulfur. Although such work should not be discouraged, it should be pointed out that the reaction of sulfur with double bonds in a material such as rubber, which is lacking in mobility, can differ considerably from the reaction with double bonds in liquid materials.

## BASIS OF THEORIES

The accumulated data obtained on the structure of rubber and on vulcanization have established a considerable amount of information to guide in

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 39, No. 7, pages 901-906, July 1947. This is the Goodyear medal lecture for 1947.

## RUBBER CHEMISTRY AND TECHNOLOGY

the formulation of theories of vulcanization. The following changes have been determined:

1. Sulfur combines chemically in an irreversible manner. The temperature coefficient of about 2.5 indicates the reaction to be chemical<sup>8</sup>. Stevens<sup>9</sup> extracted vulcanized rubber for 9 weeks with no loss of sulfur after the first week. Treatment with such materials as alkalis, litharge, or sodium will not remove the unextractable sulfur.

2. Sulfur combines in simple rubber sulfur mixtures at a fixed rate which depends on the amount of sulfur originally present, until about 70 per cent of the sulfur is combined; after that the rate decreases. Spence and Young<sup>10</sup> found that rubber containing 10 per cent of sulfur when vulcanized at 135° C reacted at the rate of about 0.46 per cent of sulfur per hour, until about 70 per cent had been added; after that the rate became reduced. When vulcanized at 155° C, the rate was about 3.4 per cent per hour until about 70 per cent had combined. The rate depends on the original amount of sulfur. Spence and Young vulcanized rubber containing 37 per cent of sulfur at 135° C and found the sulfur to combine at a rate of 1.6 per cent per hour, which is about 3.7 times the rate obtained with 10 per cent of sulfur. Most accelerators alter the addition in such a manner that the rate is not uniform<sup>11</sup>.

Although it is possible under severe conditions to cause sulfur to react with elimination of hydrogen sulfide<sup>12</sup>, it appears to add one sulfur to each double bond<sup>10</sup>. The addition of more than 32 per cent of the weight of the rubber is difficult. This amount corresponds closely to the addition of one sulfur atom to each double bond. However, there is still some doubt that all of the addition is in such a manner as to saturate double bonds<sup>13</sup>. It is possible that loss of double bond characteristics caused by change in chemical constitution could be responsible for failure of the addition agent to add to the double bond, so that double bond characteristics and not double bonds are lost.

3. The addition of sulfur destroys the elastic properties of the rubber molecule. The combination of about 8 per cent of sulfur in a rubber-sulfur mixture produces a vulcanizate of almost no strength or extensibility. Continued addition produces a horn-like consistency and finally a brittle ebonite. If the sulfur atoms are evenly spaced along the rubber molecule, the combination of 8 per cent of sulfur would mean that about twenty carbons in the chain, or five rubber units, separate the sulfur. Such rubber is of little value. Four per cent probably approaches the limit for good vulcanized rubber, which means that the minimum chain of elastic rubber must contain at least forty carbons.

4. The rate of addition of sulfur is decreased by strong acids and increased by bases while soluble zinc salts<sup>14</sup> have a neutral or a slight retarding action (Table I). Soluble zinc salts intensify the physical changes brought about by accelerators without altering the general nature of the change. The magnitude of the intensifying effect varies with different accelerators.

In a very general way the relative accelerating activity of materials increases with the basic dissociation constant. This has been shown by vulcanizing a mixture of 100 parts of smoked-sheet rubber and 6 parts of sulfur at 284° F in the presence of 1 part of various primary aromatic amines. The results are shown in Table II, which lists the dissociation constant and the amount of combined sulfur after 120 minutes of cure. The table is divided into two groups, one of which lists weak and the other strong bases.



TABLE I  
EFFECT OF MATERIAL ON RATE OF ADDITION OF SULFUR

Formula No.	A	B	C	D	E	F
Smoked sheet rubber	100	100	100	100	100	100
Sulfur	6	6	6	6	6	6
Di- <i>o</i> -tolylguanidine	..	..	1	1	..	..
Zinc oxide	..	..	..	..	..	5
Zinc propionate	..	..	..	1	1	..
Chloroacetic acid	..	1	..	..	..	..
Cure at 300° F. min.	Combined sulfur (%)					
30	0.80	..	3.50	2.75	0.63	0.48
60	1.62	0.25	4.85	4.02	1.15	1.00
90	2.15	0.34	5.06	4.48	1.60	1.76
120	3.17	0.50	5.25	4.75	2.13	2.50
180	4.10	1.33	5.52	5.22	3.75	4.08

TABLE II  
RELATION BETWEEN DISSOCIATION CONSTANT AND ACCELERATING ACTIVITY

Material	$K_b \times 10^{-3}$	Combined sulfur (%)
No accelerator		1.07
$\alpha$ -Naphthylamine	0.01	1.36
$\beta$ -Naphthylamine	0.02	1.87
Aniline	0.05	1.70
<i>m</i> -Toluidine	0.06	2.68
1,7-Naphthylenediamine	0.08	1.86
1,3-Naphthylenediamine	0.17	2.58
<i>m</i> -Phenylenediamine	0.2	1.96
<i>p</i> -Toluidine	0.2	2.40
Pyridine	0.23	0.98
Benzylamine	1,950	4.52
Allylamine	4,600	2.62
Diphenylguanidine	7,000	4.02
Di- <i>o</i> -tolylguanidine	7,000	4.34
Isoamylamine	49,000	5.42
Piperidine	120,000	4.87

Although these figures indicate a general tendency for the strong bases to be the stronger accelerators, the relation within each group is not very good, and it would be necessary to consider the structure of each compound separately to discover reasons for the difference in activity. Tertiary amines such as triethyl and tripropyl, which are strong bases, are very weak accelerators. Sulfur adds very slowly to rubber which is free of nitrogen<sup>15</sup>.

5. The resistance of vulcanized rubber to deformation does not depend on the amount of combined sulfur<sup>16</sup>. Bruni<sup>17</sup> is of the opinion that the minimum amount of combined sulfur required to initiate vulcanization is about 0.15 per cent. Such an amount will not produce more than the beginning of vulcanization. One per cent of combined sulfur may produce a high state of vulcanization if obtained in the presence of an active accelerator such as a thiuram disulfide. A high state of vulcanization cannot be obtained in the absence of accelerators with any amount of combined sulfur.

6. The physical effect of vulcanization can be overcome in most cases without alteration of the combined sulfur, and this change is reversible. It is known<sup>18</sup> that vulcanizable rubber cements accelerated with piperidinium pentamethylenedithiocarbamate gel and, if treated soon after gelation, can be re-

duced to a liquid condition by dropping more of the same accelerator on the surface of the gel. The time required for gelation increases with the original content of accelerator; this indicates that vulcanization and peptization proceed simultaneously. Oxygen seems to be a minor factor, since both gelation and peptization take place in the presence of air. The solvent is unnecessary for the action, since scorched stocks may be easily plasticized on the mill by incorporating this accelerator. Lightly vulcanized sheets of rubber which are completely insoluble in benzene can be peptized at ordinary temperature by the addition of accelerators<sup>18</sup>. The most active accelerators are generally, but not always, the most active peptizing agents. Mercaptobenzothiazole causes the rubber to go into thin solution, but mercaptobenzothiazole in the presence of a basic activator is much more rapid in its action. Soluble accelerators, such as lead oleate, are also effective. The action of accelerators differs somewhat; some cause a general swelling and disintegration, whereas a few, such as benzothiazyl disulfide, cause the rubber to dissolve from the surface, probably because the accelerator is only slightly soluble in the rubber.

Fully vulcanized rubber may be brought into thin solution in a few days at a slightly elevated temperature<sup>19</sup>. Piperidine is a sufficiently active accelerator to peptize most stocks at about 95° C. For example, rubber vulcanized with 3 parts of sulfur, 2 parts of zinc oxide, and 1 part of di-*o*-tolylguanidine to a tensile strength of 4000 pounds per square inch can be peptized to form a 5 per cent solution in toluene, which is sufficiently thin to filter rapidly through ordinary filter paper. This very low relative viscosity would, according to the Staudinger equation, indicate a low molecular weight and a greatly degraded rubber. However, the properties of the recovered rubber indicate that most of it is not in a greatly degraded condition.

The peptizing agent can be removed from such solutions by addition of alcohol. The coagulum which is thrown down still contains solvent and peptizing agent according to the partition between the rubber and alcohol. If the soft coagulum is repeatedly redissolved in benzene and reprecipitated, the peptizing agent can be effectively eliminated. Slight acidity in the alcohol favors more rapid removal of the peptizing agent.

The purified coagulum in many respects resembles polymerized chloroprene (Neoprene). Chloroprene can be polymerized until the polymerized units become too numerous; after that the units approach one another too closely, and an insoluble gel results. If the partially polymerized mass is drowned in alcohol before this stage is reached, a coagulum results which, on removal of volatile material, rapidly becomes insoluble and has vulcanized properties. In a similar manner the complete removal of solvent from the coagulum resulting from the peptized rubber produces an insoluble material with the properties of vulcanized rubber. When the sulfurized rubber molecules approach one another too closely, they cannot be separated by pure solvents. Sheets formed by evaporating pure benzene solutions will show tensile strengths of several hundred pounds per square inch. Both the Neoprene and the sulfurized rubber may again be brought into solution with peptizing agents.

#### PEPTIZATION

The peptizing of vulcanized rubber is the closest approach yet obtained to a reversal of vulcanization. In the case of Neoprene the approach is close. In the case of rubber the approach is close if we consider the combination of sulfur as being only the step preliminary to vulcanization. The reversible removal of sulfur probably cannot be accomplished.

Peptized vulcanized rubber can be separated into fractions of different consistency by fractional coagulation<sup>20</sup>. If a benzene solution is treated at slightly elevated temperature with alcohol until a slight cloudiness is developed, and if the solution is then cooled 2° or 3° and held for a few hours, the most insoluble fraction will separate as a lower layer. Successive fractions may be obtained in this manner, and finally the remainder can be obtained by complete evaporation of the liquids.

The combined sulfur is not evenly distributed among the different fractions. The most soluble fractions contain from two to three times as much sulfur as the average for the original rubber. This tendency is greatest for unaccelerated stocks. The intermediate fractions, which constitute probably two thirds of the rubber, contain less sulfur than the average for the sample. The least soluble fractions from unaccelerated stocks also contain slightly less than the average amount of sulfur. In the case of the few accelerated stocks which have been examined, the most insoluble fraction contains considerably more than the average amount of sulfur. This tendency is shown by the data in Table III,

TABLE III  
DISTRIBUTION OF COMBINED SULFUR

Fraction	Increasing softness and solubility				
	D	E	F	H	I
	Stock 1 (Unaccelerated)				
% of total rubber in fraction	38.6	23.1	30.7	6.05	1.65
% of total combined sulfur	36.4	21.9	28.2	8.00	5.55
	Stock 3 (Accelerated)				
% of total rubber	16.0	10.1	41.0	29.3	3.6
% of total combined sulfur	31.7	10.5	29.3	19.3	8.5

which was prepared from compounds 1 and 3 of Table VI in a previous article<sup>20</sup>.

#### TYPE OF COMBINED SULFUR

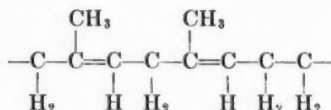
The difference in character between the different fractions of rubber indicates that sulfur combines in more than one way. This possibility has been mentioned by others<sup>21</sup>. It is probable that different types of attack exist within a single molecule of rubber. The most soluble fractions have sufficient sulfur so that they should be greatly overvulcanized if the sulfur is all combined to produce vulcanization. Instead of being stiff and brittle, the material is soft and tacky, yet still has enough elasticity to cause it to return to shape after being stretched. On the other hand, the least soluble fractions are almost entirely lacking in tackiness and resemble rubber in a high state of cure. Accelerators favor the formation of the highly vulcanized fractions either by directing the sulfur to the correct type of addition, inhibiting the degrading type of combination, or reducing the time and temperature of vulcanization, which in turn reduces the degrading type of combination. Future studies to determine the type of reaction product formed with rubber and sulfur could well include fractions of peptized rubber.

Vulcanized rubber must be a mixture heterogeneous with respect to the various sulfurized molecules of which it is composed, although it might be quite homogeneous with respect to the distribution of sulfur through the rubber mass. It must consist of an intimate interlacing mixture of the various constituents, all of which together produce the properties of vulcanized rubber.

The difference in properties between different vulcanized rubbers depends on the relative amounts and manner of assembly of the units.

The various phenomena associated with vulcanization are determined by the reactivity of the rubber molecule, which in turn is controlled by its structure and environment. The ordinarily assumed structure of rubber, consisting of condensed isoprene units with one remaining double bond for each unit, has been arrived at on the basis of the empirical formula, degree of unsaturation, x-ray spectrographs, viscosity measurements, etc. The usual picture consists of long chains of 2000 to 6000 carbon units containing regularly recurring methyl groups and double bonds at each four carbons. The chains are folded and coiled together in a more or less accidental pattern as a result of free rotation around single bonds.

Rubber resists deformation by any method such as swelling, pressing, or stretching. In the case of attack by solvents the resistance often takes the form of limited swelling, which stops when the mutual attraction of rubber molecules equals the force of solvation, and the molecules remain in disordered arrangement. When rubber is stretched, the molecules appear to orient themselves in the direction of stretching while at the same time slipping, so that sufficient double bonds lie in the same plane to produce an x-ray diffraction pattern. Partly on the evidence of this pattern we deduce the structure of the double unit of rubber to be

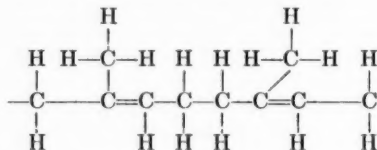


#### LACK OF DOUBLE-BOND CHARACTERISTICS

This simple picture is not adequate to account for all of the chemical properties of rubber. Among these is the lack of double-bond characteristics. Although rubber adds bromine at the double bond with some ease, it does not add chlorine first at the double bond except when attacked by strongly electrophilic chlorine donors. In other cases the chlorine first attacks a methylene carbon with liberation of hydrogen chloride. Ordinary rubber is not attacked by oxygen or ozone unless in a strained condition. This lack of reactivity is not indicated by the simple olefin structure.

The lack of double-bond characteristics of many unsaturated substances—benzene, for example—is due to resonance. Although resonance might ordinarily not be expected to contribute greatly to the stability of simple olefinic compounds, nevertheless resonance can occur and, even in such simple olefins as propene, has a definite effect on the reactivity.

The magnitude of the stabilizing influence of resonance can often be estimated by means of the heat of combustion. Several workers<sup>22</sup> have determined the heat of combustion of rubber, the most recent being Jessup and Cummings. They found a value of 45,274 joules per gram of purified rubber, which is equivalent to 1470 kg.-cal. for the double unit



Data are also available for the calculation of the heat of combustion based on bond contributions<sup>23</sup>. Since the molecular weight of the rubber molecule and the condition of the terminal groups are uncertain, it is necessary to base the calculation on a central portion of the molecule. For this purpose this double unit was used. The calculation is shown in Table IV.

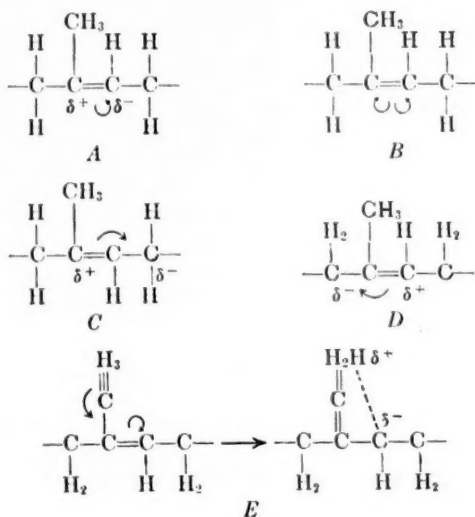
TABLE IV  
HEAT OF COMBUSTION OF RUBBER

Type of bond	Bond contribution (kg.-cal.)	No. of bonds	Contribution (kg.-cal.)
C—H	53.3	16	852.8
C—C	50.8	8	406.4
C=C	118.8	2	237.6
		Heat of combustion	1496.8

These figures are not directly comparable, because the calculated figures are based on gaseous material. It will be necessary to add to the determined value the heat of vaporization of a double unit of rubber. No such data are available, but most hydrocarbons have a value of less than 100 calories per gram; for example, the heat of vaporization of hexylene is 93.5 calories per gram. If the combustion figure is corrected at the rate of 100 calories per gram, it would become  $1470 + 13.6$  or 1483.6 kg.-cal., leaving a difference of only 13.2 kg.-cal. per double unit of rubber as the resonance energy. This is an indicated resonance energy of 0.92 per cent of the heat of combustion. Although heats of combustion can be determined with greater accuracy than this, the resonance energy is so small that the result can be considered only as indicative.

#### RESONATING STRUCTURES

Various resonating structures can be shown for rubber. Since olefin bonds are characteristically nucleophilic, and the double bond in rubber seems to be no exception, the important structure must be one which can produce a high electron density at some point. The following structures illustrate some of the possible conditions of resonance:



Since the rubber molecule is entirely hydrocarbon, it would not be expected to have any points of great permanent electron density. Such points of electron density appear only by an electromeric displacement under the influence of an external field such as might be supplied by an attacking agent.

In discussing the various structures, the chain carbons will be numbered from left to right. Structure *A* produces an increased electron density on carbon 3, which acquires a fraction negative charge. Under extreme conditions the 3 carbon could have a formal charge of  $-1$ , and the 2 carbon would act as a strongly electrophilic point with a formal charge of  $+1$ . Such a condition must occur so infrequently as to be unimportant. In those cases where the demand for electrons on the 3 carbon is very great, it is improbable that the total demand is met by the 2 carbon but rather by a shift which affects other centers as well. In this way a relatively high nucleophilic point may be obtained without the production of a correspondingly high electrophilic point. The grouping about the double bond would become polar and electrophilic reagents could attack, but nucleophilic reagents would be ineffective.

Structure *B* is a type usually associated with activated gases. This shift would not create polarity and would not be induced by an external field. It is probably of no importance in the rubber molecule.

Structure *C* is also a latent polarity (polarizability) effect, which can become important under the demand of an external field. In this case the 4 carbon in the methylene group becomes activated. Dehydrogenation reactions should be favored. The arrow points to the right of the double bond because the effect of the methyl group attached to the 2 carbon in conjunction with the double bond should favor a shift in this direction. The analogous structure *D* is probably much less important than structure *C*.

Some evidence exists that an electromeric shift to activate methylene groups is the most prevalent type in normal rubber. Chlorine first attacks rubber to form substitution products, with the elimination of hydrogen chloride, and only by the use of such chlorinating agents as sulfuryl chloride is the attack first at the double bond. This might indicate that the latent polarity due to hyperconjugation is capable of very great development on the proper demand but that, in the presence of less intense field effects, the greater electron density appears on the methene carbon.

Structure *E* represents a condition that can exist in natural rubber but not in polymers of unsubstituted butadiene. It is well known that the methyl group is capable, on demand, of electron release, and this effect can become pronounced in connection with doubly bonded carbon; for example, hyperconjugation between the methyl group and the double bond of propene produces a resonance energy approximately the same as that produced in butadiene by two conjugated double bonds. Hyperconjugation in the rubber molecule should, under the influence of an external field, make possible a considerably increased electron density on the 3 carbon. This seems to be the most likely point of attack by an electrophilic reagent with sufficient field intensity and the one by which the latent polarity could be most highly developed.

#### POSTULATION OF RUBBER PHENOMENA

On the basis of the resonating forms, it is possible to postulate many of the phenomena displayed by rubber. It is first necessary to recognize that the rubber unit is not symmetrical, and for that reason a different sequence occurs



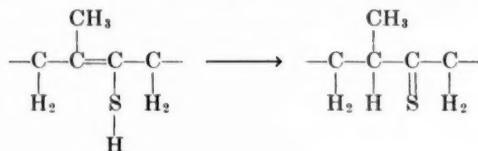
in passing along the carbon chain in different directions. In one direction the double bond precedes the methyl group, whereas in the other direction the reverse is true. It is reasonable to assume that in the rubber mass approximately an equal number of molecules lie in each direction. Since the rubber units possess latent polarity, this might be developed to a minor extent by the proximity of two reverse resonating units.

Such an occurrence in a semisolid material would be more or less permanent, because the associated units could not trade partners as is possible in mobile liquids. This increased resonating state could account for the reduced double bond characteristics of rubber. This type of resonance comes into effect only on demand, and the proximity of a unit in the same position could have no effect. This means that, on stretching, the various units should seek out positions such that alternate layers of reversed polarity would result and an increasingly ordered arrangement of the molecules would be obtained. For this reason racked rubber should produce an x-ray fiber pattern. The attractive force is sufficient to maintain racked rubber in an extended position until the vibrational energy of the rubber molecules is increased by raising the temperature.

Ordinary rubber is known to be very resistant to oxidation under ordinary conditions. However, when rubber is placed under strain on a rubber mill, it rapidly oxidizes and becomes more plastic. It is difficult to believe that all the resonating centers in rubber would be paired; oxygen would be expected to attack unpaired centers but is unable to do so. The heavier sulfur atom is capable of attack. Perhaps the field effect of the oxygen in conjunction with the small activation remaining as paired resonating units are being separated is sufficient to initiate attack. Whether the attack once completed actually ruptures the carbon chain or merely destroys the resonating center is not known. No evidence exists to show that either the latent or permanent polarity of the rubber is altered.

Sulfur attacks rubber probably in one of the resonating forms *C* or *E*. In the first case, which may be important in the absence of accelerators, the attack would tend to replace hydrogen from the 4 methylene carbon to form either a sulfhydryl group or to eliminate hydrogen sulfide. Two carbons which might be in the same or different molecules could be united by means of sulfur. If carbons are united, the probability is greatly in favor of uniting two molecules. The attack on the 3 carbon of form *E* is probably the most important under vulcanizing conditions. The attack should be retarded by strongly electrophilic substances, such as strong acids, and should be assisted by nucleophilic substances, such as bases, unless the latter reacts to form relatively stable sulfur compounds.

The result of attack on the 3 carbon is not clear. The first step might form the mercaptan, which would be the desmotrope of the corresponding thioketone.



Such an arrangement would result in a permanent dipole and would maintain an active methylene group as a point of attack for more sulfur. Thioketones of low molecular weight are very active and polymerize readily to form ring

structures containing sulfur bridges. Such products are usually trimers, although other polymers are known.

In spite of all the speculation and investigation into the manner of addition of sulfur, the problem is not yet solved. One of the most important contributions to the study is that of Selker and Kemp<sup>24</sup>, who have reacted vulcanized rubber with methyl iodide. They conclude that a considerable amount of sulfide sulfur is present. This would indicate the linking of carbon atoms either inter- or intramolecularly by sulfur. Farmer<sup>25</sup> believes the presence of episulfides is unlikely. Thioketones also are reactive with methyl iodide and might be included in the sulfide sulfur determination. Paired dipoles containing thioketones could also unite by hydrogen bonding. Regardless of the nature of the attack, the result is that the reaction product becomes definitely polar and appears to have predominantly electrophilic properties.

The sulfur in simple rubber-sulfur mixtures combines at a constant rate which depends on the original concentration of sulfur. Various explanations, such as consecutive reactions, chain reactions, autocatalytic reactions, and micelle disaggregation, have been suggested as the controlling factor. The presence of predominantly electrophilic dipoles in the rubber might activate other unsaturated groups in the immediate vicinity to facilitate attack by other sulfur. It is reasonably certain that attack of the 3 carbon by sulfur, especially if a thioketone group resulted, would activate the methylene carbon next to it. The remaining methylene groups between this and the double bond in the next group would in turn become somewhat more active. In this manner the reaction with sulfur would become more rapid as the attack on double bonds increased, and the rate of reaction could be maintained although the concentration of sulfur continued to decrease.

#### RATE OF COMBINATION OF SULFUR

The presence of combined sulfur is sufficient to cause an increase in the rate of combination of sulfur. A uniform blend of smoked sheets was used for the following experiment. Acetone-extracted rubber was compounded with 6 parts of sulfur and vulcanized. It was then thoroughly acetone-extracted, and the combined sulfur was determined. This extracted rubber was then compounded with 6 parts of sulfur. A second compound was prepared from 100 parts of extracted smoked sheets and 6 parts of sulfur, and the two compounds were cured in the same mold for 2 hours at 140° C. Each compound was then extracted and the combined sulfur determined. The results in Table V show that the presence of combined sulfur has accelerated the further

TABLE V  
INFLUENCE OF COMBINED SULFUR ON COMBINATION OF SULFUR

Original	Combined sulfur (%)		Relative rate of combination
	Final	Increase	
0.0	2.65	2.65	1.00
1.73	5.24	3.51	1.32

combination of sulfur. Since the combination of sulfur takes place at a uniform rate, it is assumed that the initial rate of addition is indicated closely by a measurement taken when only about half of the sulfur has been consumed.

The following calculation can be made from the data of Table V. If we consider the concentration of rubber to remain constant in the reaction  $R + S$

= RS, the rate of reaction varies with the concentration of sulfur. If 1.73 grams have combined in the fresh rubber compound, the concentration of dissolved sulfur is 4.27 grams, and the relative rate of combination should be reduced to  $4.27/6 = 0.71$  of the initial rate. Since 1.73 per cent of combined sulfur in the present case has increased the rate by the factor 1.32, the rate should be  $1.32 \times 0.71 = 0.94$ , or the rate should be approximately the same as at the beginning.

#### ACTION OF ACCELERATORS

If sulfur combines with rubber because certain points acquire a sufficient electron density, then the primary action of accelerators must be on the rubber. Since the electron density is created only under the field of a sufficiently electrophilic attacking reagent, the action of the accelerator must be simultaneous with, but cannot precede, that of the sulfur. It could be possible for accelerators which are sufficiently nucleophilic to be less efficient because of competition with rubber in the reaction with sulfur. Such accelerators, which would usually be the more basic ones, would not be preferred for use in low sulfur compounds. Accelerators should assist the release of electrons from the methyl group and promote the electron shift shown in structure *E*.

The action of soluble zinc salts is still speculative. Insoluble zinc salts seem to be quite ineffective. Soluble zinc salts in the absence of natural or added acceleration appear to have little effect or to have a slight retarding effect of vulcanization. It seems evident that the answer lies somewhere in the mutual or combined effect of accelerator and zinc salt. Perhaps the answer in some cases lies in the formation of Werner-type complexes which regulate the nucleophilic properties in the desired range. Cadmium and sometimes mercury, when substituted for zinc, produce activation but in different degrees. Indications exist that zinc cannot be removed completely from vulcanizates without destroying them, and further indications have been found<sup>18</sup> of a condensing or polymerizing effect of zinc salts.

No adequate theory of vulcanization has yet been advanced and probably will not be until better information in regard to the manner of combination of sulfur is available. The apparent presence of sulfide sulfur is strongly indicative of cross-linking of the various molecules by means of sulfur, and yet sulfide sulfur could be present without cross-linking. If the sulfur first attacks a methylene carbon, the most probable result would be the formation of a sulfhydryl group, and coupling could take place only by oxidation. If a doubly bound carbon of paired bonds is attacked to form a thioketone, bonding might take place by polymerization between two such bonds. If paired bonds are attacked to form any permanently polar structure, the linking between molecules may consist of nothing more than the pairing of such more strongly polar structures. It seems most logical that any intramolecular bonding must take place at the olefinic points and that any sulfuration of methylene carbons is purely destructive. Methylene attack probably is most rapid when accelerator influence is absent, as in unaccelerated stocks or on overcure with expendable accelerators. In this connection the data of Table VI, taken from the previous paper<sup>29</sup>, are of interest.

The stocks containing no added accelerator have very little increased stiffness, which shows that most of the sulfur has combined in an ineffective manner. The combined sulfur in the accelerated stock has produced a high stiffness which increases with the combined sulfur; this indicates that much of this sulfur has

TABLE VI

RELATION BETWEEN COMBINED SULFUR AND PHYSICAL PROPERTIES<sup>20</sup>

Accelerator	Tensile strength at 700% elongation (lb. per sq. in.)	Combined sulfur (%)
None, 60-min. cure	175	1.92
None, 120-min. cure	375	3.85
Butyraldehyde butylamine	4000	2.38
Di- <i>o</i> -tolylguanidine	3600	2.25
Tetramethylthiuram disulfide	1875	0.34

produced bonding. Of the three stocks, the softest one cannot be peptized with piperidine; this indicates a greater possibility of covalent bonding rather than association through dipoles or hydrogen bonds.

The ability of nucleophilic materials to peptize rubber in benzene solution is an indication of association through paired dipoles. Since the dipole is essentially electrophilic—that is, the electron deficiency is more localized than the density—the dipolar attraction can be overcome by the presence of a more strongly nucleophilic substance. Upon the removal of such substance, many of the paired poles can again reform, and the rubber is once more firm and insoluble. The activity of peptizing agents may be quite different from their accelerating activity.

The study of vulcanization should be encouraged particularly because of its importance to the synthetic rubber industry. The natural rubber industry developed as an art largely because of the adaptability of the natural product. Most synthetic rubbers, other than chloroprene polymers, refuse to vulcanize satisfactorily in the absence of large amounts of various powders. Perhaps the present synthetics will be vulcanized satisfactorily in the future. It is certain that a better understanding of the process by which natural rubber is vulcanized would assist in finding better methods of vulcanizing synthetics and in the formulation of synthetics which are more vulcanizable.

## REFERENCES

- <sup>1</sup> Henriques, *Chem.-Ztg.* **17**, 634 (1893); **18**, 701, 1155 (1894).
- <sup>2</sup> Weber, *Kolloid-Z.* **1**, 33, 65 (1906).
- <sup>3</sup> Stern, *Chem. Ztg.* **33**, 756 (1910).
- <sup>4</sup> Hübener, *Z. angew. Chem.* **7**, 112, 142 (1894).
- <sup>5</sup> Höhn, *Gummi-Ztg.* **14**, 17 (1899).
- <sup>6</sup> Ostwald, *Kolloid-Z.* **6**, 136 (1910).
- <sup>7</sup> Meyer and Hohenemser, *Helv. Chim. Acta* **18**, 1061 (1935); RUBBER CHEM. TECH. **9**, 201 (1936); Jones and Reed, *J. Am. Chem. Soc.* **60**, 2452 (1938); Hauser and Sze, *J. Phys. Chem.* **46**, 118 (1942); RUBBER CHEM. TECH. **15**, 560 (1942); Armstrong, Little and Doak, *Ind. Eng. Chem.* **36**, 628 (1944); RUBBER CHEM. TECH. **17**, 788 (1944).
- <sup>8</sup> Spence and Young, *Kolloid-Z.* **11**, 28 (1912); *Chem.-Ztg.* **36**, 1162 (1912); Twiss and Brazier, *J. Soc. Chem. Ind.* **39**, 125T (1920); Sheppard, *India Rubber World* **80**, No. 2, 56 (1929); Park, *Ind. Eng. Chem.* **22**, 1004 (1930); Maxwell and Park, *Ind. Eng. Chem.* **24**, 148 (1932); Sandstrom, *Ind. Eng. Chem.* **25**, 684, 1400 (1933).
- <sup>9</sup> Stevens, *J. Soc. Chem. Ind.* **38**, 192T (1919).
- <sup>10</sup> Spence and Young, *Kolloid-Z.* **11**, 28 (1912); *Chem.-Ztg.* **36**, 1162 (1912).
- <sup>11</sup> Twiss and Brazier, *J. Soc. Chem. Ind.* **39**, 125T (1920); Whitby and Simmons, *Ind. Eng. Chem.* **17**, 931 (1925); Hardman and White, *Ind. Eng. Chem.* **19**, 1037 (1927).
- <sup>12</sup> Stevens and Stevens, *J. Soc. Chem. Ind.* **48**, 55T (1929); **50**, 397T (1931); Fisher and Schubert, *Ind. Eng. Chem.* **28**, 209 (1936).
- <sup>13</sup> Brown and Hauser, *Ind. Eng. Chem.* **30**, 1291 (1938); RUBBER CHEM. TECH. **12**, 4 (1939); Thornhill and Smith, *Ind. Eng. Chem.* **34**, 218 (1942); RUBBER CHEM. TECH. **15**, 272 (1942).
- <sup>14</sup> Brown and Hauser, *Ind. Eng. Chem.* **30**, 1291 (1938); RUBBER CHEM. TECH. **12**, 4 (1939).
- <sup>15</sup> Beadle and Stevens, *Kolloid-Z.* **11**, 61 (1912); **12**, 46 (1913); Stevens, *Kolloid-Z.* **14**, 91 (1914).
- <sup>16</sup> Shepard and Krall, *Ind. Eng. Chem.* **14**, 951 (1922); Hardman and White, *Ind. Eng. Chem.* **19**, 1037 (1927); Brown and Hauser, *Ind. Eng. Chem.* **30**, 1291 (1938); RUBBER CHEM. TECH. **12**, 4 (1939).
- <sup>17</sup> Bruni, *Rev. gén. caoutchouc* **8**, No. 75, 19 (1931).
- <sup>18</sup> Williams, *Ind. Eng. Chem.* **26**, 1190 (1934); RUBBER CHEM. TECH. **7**, 102 (1934).
- <sup>19</sup> Williams, *Proc. Rubber Tech. Conf. London, 1938*, 304; RUBBER CHEM. TECH. **12**, 191 (1939); Farmer, "Advances in Colloid Science", New York, 1943, Vol. 2, p. 342.
- <sup>20</sup> Williams, *Proc. Rubber Tech. Conf. London, 1938*, p. 304; RUBBER CHEM. TECH. **12**, 191 (1939).

- <sup>21</sup> Brown and Hauser, *Ind. Eng. Chem.* **30**, 1291 (1938); RUBBER CHEM. TECH. **12**, 4 (1939); Selker and Kemp, *Ind. Eng. Chem.* **36**, 27 (1944); RUBBER CHEM. TECH. **17**, 303 (1944).
- <sup>22</sup> Kirkoff and Matulke, *Ber.* **57B**, 1266 (1924); Messenger, *Trans. Inst. Rubber Ind.* **5**, 71 (1929); RUBBER CHEM. TECH. **3**, 24 (1930); Blacke, *Ind. Eng. Chem.* **22**, 737 (1930); RUBBER CHEM. TECH. **3**, 63 (1930); Jessup and Cummings, *J. Research Natl. Bur. Standards* **13**, 357 (1934).
- <sup>23</sup> Wheland, "Theory of Resonance", John Wiley & Sons, New York, **1944**, p. 64.
- <sup>24</sup> Selker and Kemp, *Ind. Eng. Chem.* **36**, 27 (1944); RUBBER CHEM. TECH. **17**, 303 (1944).
- <sup>25</sup> Farmer, "Advances in Colloid Science", New York, **1943**, Vol. 2, p. 342. Other references worthy of attention in connection with the subject are: Curtis, McPherson and Scott, *Bur. Standards, Sci. Paper No. 560*, 398 (1927); Farmer and Shipley, *J. Polymer Sci.* **1**, 293 (1946); Naylor, *J. Polymer Sci.* **1**, 305 (1946); Bloomfield, *J. Polymer Sci.* **1**, 312 (1946).

## SULFUR LINKAGE IN VULCANIZED RUBBER

### REACTION OF SULFUR WITH 2-METHYL-2-BUTENE \*

MILTON L. SELKER AND A. R. KEMP  
BELL TELEPHONE LABORATORIES, MURRAY HILL, N. J.

Year by year the complete definition of vulcanized rubber in terms of organic chemistry has become more desirable. The severity of the demands on rubber products makes it imperative to extend basic knowledge of vulcanization if we are to overcome the traditional defects or use limitations in this field.

Chemical investigations of the vulcanization problem can be arranged into three lines of attack. In the first method the vulcanizate network is severed at various points by chemical or thermal means to liberate small portions of the material which can be studied as are small molecules. Ideally there should be no alteration of the linkages except where cutting of the chains takes place. Unfortunately no such "scissors" are known. Midgley, Henne, and Sheppard<sup>1</sup> applied the thermal decomposition method to ebonite. Their study of the fragments, based on 1 per cent of the total material involved, was inclusive.

Secondly, a small molecule reagent which swells the rubber may be used to penetrate the three-dimensional network and react with the various linkages in it. This method was used by Meyer and Hohenemser<sup>2</sup>, who diffused methyl iodide into vulcanized rubber. This complicated reaction and its background with pure sulfur compounds were reported in the first two articles in the present series<sup>3</sup>. The conclusions of this study were that the part of the combined sulfur which could be removed as trimethylsulfonium iodide was sulfide sulfur linked to a carbon atom alpha to a double bond. In most cases the less of this type of sulfur present, the higher the tensile strength of the vulcanizate. Methyl iodide was successful to a hitherto unattained degree because both its rate of reaction and products vary with the type of sulfur bond. This work left unanswered the question of the sulfur linkages which were not attacked by methyl iodide—in some cases the greater part of the combined sulfur.

The third chemical line of attack is the study of model systems. A small molecule, such as an olefin, is reacted with sulfur and rubber-compounding ingredients; then, from identification of the products and study of the reaction, conclusions concerning vulcanizates are reached by analogy. The use of this method is old in chemical problems.

In 1916 Friedmann<sup>4</sup> first used the reaction of simple hydrocarbons with sulfur in an effort to find out more about the origin of the sulfur compounds in Mexican petroleum. It was not until 1935 that Schwarzkopf<sup>5</sup> proposed the use of model systems for the study of rubber vulcanization. His choice of ethyl cinnamate was somewhat unfortunate, as it is not a very close parallel to rubber structure.

In 1944 Armstrong, Little, and Doak<sup>6</sup> published the results of a great deal of work on the reaction of sulfur alone and with compounding ingredients, on

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 39, No. 7, pages 895-900, July 1947. This paper was presented before the Division of Rubber Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, New Jersey, April 10-12, 1946.



the olefins 2-methyl-2-butene, 2-methyl-1-butene, 2-butene, cyclohexene, and 5-methyl-4-nonene. They concluded that "sulfur vulcanization of rubber is due chiefly to the formation of disulfide and monosulfide cross-links, which are attached to the  $\alpha$ -methylene group or the  $\alpha$ -methyl group of the rubber chain".

#### REACTION OF 2-METHYL-2-BUTENE WITH SULFUR

The reaction of 2-methyl-2-butene and sulfur was carried out in glass pressure flasks. After proper time at low temperatures to encourage crystallization of sulfur and solid products, the bomb was opened, the unreacted olefin was stripped off under vacuum, and the sulfur products were put through a molecular still. As much product was removed as was possible at room temperature.

To ensure that very little of the sulfur itself would remain dissolved in the reaction mixture, the solubility of sulfur in 2-methyl-2-butene was investigated. It is 0.73 and 0.18 per cent at 30° and 4° C, respectively. In allyl disulfide the solubility was 2.50 and 1.37 per cent at 26° and 4° C, respectively. Thus some sulfur would be left in the reaction mixture even if it stood at 0° C for some time. For this reason it is preferable to hold the reaction bulb at -78° C for some days after the reaction before opening, to crystallize all the solid products. The reactants, conditions, and pertinent data for the seven runs made with 2-methyl-2-butene are given in Table I. Table II gives the detailed analysis of the products of each run.

TABLE I  
REACTION OF 2-METHYL-2-BUTENE WITH SULFUR AT 141.6° C

Run	Original sulfur (%)	Time (hrs.)	Sulfur reacted (%)	Olefin reacted (%)	Reaction mixture	
					Liquid color	Solids
1†	7.00	1	19.2	3	Pale yellow	Sulfur needles
2	7.20	2	46.3	4	Light yellow	Sulfur needles
3	7.12	4	93.7	8	Light orange	Yellow-green rhombic sulfur
4	7.59	8	100	11	Orange-red	None
5	9.25	24	100	20	Dark red	0.7 C <sub>8</sub> H <sub>16</sub> S <sub>2</sub> ‡, §
6	32.6	24	100	73	Black-red	1.47 C <sub>8</sub> H <sub>16</sub> S <sub>2</sub> ‡, yellow-brown
7	31.8	32	100	77	Black	3.22 C <sub>8</sub> H <sub>16</sub> S <sub>2</sub> ‡, brown-black

\* Percentage of total sulfur that reacted.

† Inadequate shaking; reactional rate is somewhat slow.

‡ Percentage of total sulfur-containing products.

§ In solution.

Reaction times of over 4 hours do not give any solid residue of unreacted sulfur in the bomb. Run 4, for instance, has no solid in the cooled reaction vessel. In runs 2 and 3, where unreacted sulfur remained, the small amount of dissolved sulfur in the stripped reaction products came over in the molecular distillation. The crystals indicated in run 2, fractions 3 and 4, and in run 3, fractions 4 and 5 (Table II) are sulfur. They were isolated and identified by analysis.

However, in runs 6 and 7 a solid is again present in the cooled reaction bomb. This solid was yellow-brown in run 6 and brown-black in run 7. Examined under the microscope, the crystals of run 6 were yellow thick columns. The run 7 solids product was composed of two types of material, yellow needles and black spherulites. These materials are the hydrogen-poor products discussed below.

In runs 5 and 6 no attempt was made to crystallize these solid products in the unopened bond. Consequently the hydrogen-poor solid products of these

TABLE II  
ANALYSIS OF PRODUCTS

Run	Fraction	Bath. temp. (° C)	Per cent	Color	State (L = Liquid, C = Crystals)	C/H	H (%)	C (%)	S (%)	Total (%)	Mol. wt.	$n_D^{25}$
1 (1 hr.)	1	40	42.2	Yellow	L { Calcd. for $C_{10}H_{12}S_4$	..	..	..	50.9	..	230	..
	2	>40	57.8	Yellow-orange	L (viscous)	..	..	..	50.6	..	237	1.6638
	1	23	1.3	Light yellow	L	..	..	..	51.6	..	430	1.5779
	2	29	26.5	Yellow	L { Calcd. for $C_{10}H_{12}S_{4.4}$	5.80	6.4	36.8	56.3	99.5	228	1.6060
2 (2 hr.)	3	30	24.3	Yellow	L { Calcd. for $C_{10}H_{12}S_{4.7}$	5.79	6.4	37.2	56.4	..	323	..
	4	33-140	31.7	Red-orange	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	58.4	..	248	1.6187
	5	>140	1.2	..	L	5.68	6.1	34.6	59.1	..	336	..
	6	..	2.3	..	L	5.67	6.1	34.4	59.6	..	305	1.6355
3 (4 hr.)	Residue Trap On condenser	..	2.3	..	L	..	..	..	..	..	..	..
	Loss	..	3.5	..	L	..	..	..	..	..	..	..
	1	31	14.3	Yellow	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	..	..	..	..
	2	31	16.4	Yellow-gold	L { Calcd. for $C_{10}H_{12}S_{4.1}$	5.95	6.89	40.95	47.5	95.4	180	1.5670
4 (8 hr.)	3	31	13.6	Yellow-gold	L { Calcd. for $C_{10}H_{12}S_{4.1}$	5.86	6.49	38.1	47.5	..	269	..
	4	31-80	7.01	Gold	L { Calcd. for $C_{10}H_{12}S_{4.1}$	5.87	6.66	39.1	54.2	98.9	236	1.6001
	5	90	10.8	Gold	L { Calcd. for $C_{10}H_{12}S_{4.1}$	5.76	6.50	37.45	55.4	99.4	225	1.6042
	6	140	0.79	Red	L { Calcd. for $C_{10}H_{12}S_{4.1}$	5.78	6.54	37.85	55.6	..	317	..
5	Residue Trap Loss	..	6.2	Black	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	55.3	..	255	1.6160
	1	>140	0.51	Light yellow	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	99.1	..	319	1.6127
	2	30	3.1	Red	L { Calcd. for $C_{10}H_{12}S_{4.1}$	5.90	5.91	34.95	58.7	..	307	1.6308
	3	30	32.4	Yellow-gold	L (viscous)	5.90	6.00	35.45	58.5	99.6	339	..
6	4	35-90	7.2	Orange	L (light)	..	..	..	..	..	..	..
	5	90-140	31.2	Red-Black	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	..	..	..	..
	6	..	6.9	..	L	..	..	..	..	..	..	..
	7	..	32.4	Yellow-gold	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	..	..	..	..
7	8	30	18.4	Orange	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	44.6	..	211	1.5595
	9	31	..	..	L	..	..	..	51.3	..	253	1.5649
	10	31	..	..	L	..	..	..	51.1	..	245	1.5860
	11	31	..	..	L	..	..	..	50.5	..	285	..
8	12	35-90	7.2	Orange	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	50.5	..	270	1.5868
	13	90-140	31.2	Red-Black	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	51.4	..	326	1.5977
	14	..	..	..	L	..	..	..	51.4	..	292	..
	15	..	..	..	L { Calcd. for $C_{10}H_{12}S_{4.1}$	..	..	..	51.6	..	..	..



runs were recovered as solids plus some liquid, on the condenser of the molecular still with the pot at room temperature (Table II, run 5, fraction C, and run 6, fraction 2S). This was possible only because the condenser temperature was  $-78^{\circ}\text{C}$ . If tap water had been used instead, the solubility of the solid products in the liquid products was high enough so that no solid would have been detected in the condensate at all. In run 7 an effort was made to freeze out all the solid product by leaving the unopened bomb at  $-78^{\circ}\text{C}$  for 7 days. This was successful, and very little additional solid was obtained by molecular distillation of the reaction mixture. These solids are fairly insoluble in petroleum ether at  $-78^{\circ}\text{C}$ , so they could be detected in the liquid hydrogen-rich products by diluting these fractions with 3 volumes of cold petroleum ether, cooling to  $-78^{\circ}\text{C}$ , and filtering off the precipitated solids.

In several runs the recovered unreacted olefin was carefully fractionated. Only traces of lower boiling hydrocarbons were found. Therefore no appreciable isomerization of the olefin takes place in these reactions.

The products of the reaction are liquids of polysulfide type  $\text{R-S}_x\text{-R}$ , where  $x$  varies from 2 to 6 and R is an alkyl or alkenyl group and solids, two of which,  $\text{C}_5\text{H}_6\text{S}_3$  and  $\text{C}_{10}\text{H}_{10}\text{S}_3$ , have been isolated. The former group is referred to as the hydrogen-rich product and the latter, the hydrogen-poor product.

#### HYDROGEN-RICH PRODUCTS

The carbon and hydrogen analyses in Table II show that, in general, the hydrogen content of the liquids of type formula  $\text{R-S}_x\text{-R'}$  is somewhat higher than could be expected by reaction of two  $\text{C}_5\text{H}_{10}$  molecules. Whether this hydrogen excess is real only further careful work will decide. If it is real, hydrogen transfer is indicated; this theory is supported by the presence of the two hydrogen-poor solid compounds,  $\text{C}_5\text{H}_6\text{S}_3$  and  $\text{C}_{10}\text{H}_{10}\text{S}_3$ . Also noteworthy is the fact that the highest polysulfides tend to have hydrogen contents  $\text{H}_{21}$ , whereas the lower ones tend to  $\text{H}_{20.5}$ .  $\text{H}_{22}$  would result from two saturated residues, whereas  $\text{H}_{20}$  results from one saturated and one unsaturated group.

The empirical formulas of the type  $\text{C}_{10}\text{H}_{20.6}\text{S}_x$  and  $\text{C}_{10}\text{H}_{21}\text{S}_x$  given in Table II suggest that these fractions could be mixtures of the compounds  $\text{C}_{10}\text{H}_{18}\text{S}_x$ ,  $\text{C}_{10}\text{H}_{20}\text{S}_x$ , and  $\text{C}_{10}\text{H}_{22}\text{S}_x$ . The higher, initially formed polysulfides appear to have more saturated residues than do the lower polysulfides. The shorter the time of reaction, the higher the polysulfide formed. This is shown by consideration of Table II where, for the 2-hour reaction, 81 per cent of the product is higher than  $\text{—S}_{5.7}\text{—}$ , for the 4-hour run 50 per cent is above  $\text{—S}_{5.5}\text{—}$ , and for the 8-hour run no higher product than  $\text{—S}_{4.5}\text{—}$  is isolated.

Fractions 1, 2, 3, and 6 of run 3 were reacted with methyl iodide according to the standard procedure<sup>3</sup>. The results are shown in Table III. The methyl iodide reaction shows that the amount of dialkenyl polysulfide is greatest in the volatile fraction 1 with some in 2 but none in fractions 3 and 4. More iodine should be liberated, but it is probably taken up by the sulfur linkages and the carbon-carbon double bonds. Fractions 3 and 6, therefore, may contain alkylalkenyl polysulfides and(or) dialkyl polysulfides. The mercuric iodide-catalyzed reaction with methyl iodide confirms this by showing but few crystals of  $(\text{CH}_3)_3\text{SI}\cdot\text{HgI}_2$ , which results with dialkenyl disulfides, but much iodine and an oily layer; the latter probably contains products of the type dimethyl alkyl sulfonium iodide  $\cdot\text{HgI}_2$ , where the alkyl is an amyl group of some type. The terms alkenyl sulfide, etc., include only those unsaturated residues in which the sulfur linkage is alpha to the double bond.

TABLE III  
 REACTION OF RUN 3 POLYSULFIDES WITH METHYL IODIDE AT 24° C

Frac- tion	Formula	CH <sub>3</sub> I Reaction			CH <sub>3</sub> I + HgI <sub>2</sub> Reaction		
		Time (Hr.)	Crystals, (CH <sub>3</sub> ) <sub>2</sub> SI	Moles I <sub>2</sub> /mole compound	Crystals, (CH <sub>3</sub> )SI <sub>2</sub> · HgI <sub>2</sub>	Moles I <sub>2</sub> /mole compound	Oil product (red-brown)
1	C <sub>10</sub> H <sub>20</sub> S <sub>4</sub>	24	Many	..	Many	..	Much
1	C <sub>10</sub> H <sub>20</sub> S <sub>4</sub>	190	Many	0.07	Many	0.51	Thick deposit
2	C <sub>10</sub> H <sub>20.2</sub> S <sub>6.2</sub>	24	Small	..	Some	..	Some
2	C <sub>10</sub> H <sub>20.2</sub> S <sub>6.2</sub>	190	Some	0.04	Many	0.85	Much
3	C <sub>10</sub> H <sub>20.6</sub> S <sub>6.6</sub>	24	None	..	Few	..	Little
3	C <sub>10</sub> H <sub>20.6</sub> S <sub>6.6</sub>	190	Small	0.02	Fair	0.93	Fair amount
6	C <sub>10</sub> H <sub>20.6</sub> S <sub>6.2</sub>	24	None	..	Very few	..	Little
6	C <sub>10</sub> H <sub>20.2</sub> S <sub>6.2</sub>	190	None	0.02	Some	1.14	Fair amount

## HYDROGEN-POOR PRODUCTS

The hydrogen-poor products are found only in small quantities in the reaction mixture on long heating. Two compounds have been isolated: C<sub>5</sub>H<sub>6</sub>S<sub>3</sub>, yellow needles, analysis given in Table II, run 6, fraction 2S; C<sub>10</sub>H<sub>10</sub>S<sub>3</sub> (?), brick-red needles, melting point 197° C, analysis 51.9% C, 4.69% H. Since only about 8 mg. of the higher melting compound was isolated, no extensive purification was possible, and the empirical formula given is tentative. Enough of the lower melting compound, C<sub>5</sub>H<sub>6</sub>S<sub>3</sub>, was purified and available for carrying out various reactions.

A search of literature revealed one compound of the formula C<sub>5</sub>H<sub>6</sub>S<sub>3</sub>. Barbaglia<sup>7</sup> in 1884 had prepared it from isovaleraldehyde.

This reaction was repeated. A yellow-orange crystalline compound (melting point, 95.0° C) was isolated from the liquid reaction products. The C<sub>5</sub>H<sub>6</sub>S<sub>3</sub> from sulfur reaction with 2-methyl-2-butene had a melting point of 95.2° C. The mixed melting point was 95.1° C. Therefore the same compound, C<sub>5</sub>H<sub>6</sub>S<sub>3</sub>, results from action of sulfur with isovaleraldehyde as with 2-methyl-2-butene. The sulfur linkage on the terminal carbon atom in the 4 position of the 2-methylbutane carbon skeleton, which is suggested by the preparation of C<sub>5</sub>H<sub>6</sub>S<sub>3</sub> from isovaleraldehyde, fits in with the structure supported by the evidence to follow.

*Reaction of sulfur with isovaleraldehyde.*—16 grams of sulfur with 32 grams of Eastman White Label isovaleraldehyde were sealed *in vacuo* in a Carius tube. Reaction at 240° C for 10 hours gave a red-black liquid with some black crystalline residue. Distillation of liquid gave 4 cc. water-white liquid, boiling point 82° C; 17 cc. yellow liquid, b.p. 169–175° C; 20 cc. orange liquid, b.p. 175–185° C; and 4 cc. black tar. The orange liquid gave yellow-orange crystals on cooling to –30° C. Recrystallization from ethanol at –30° C gave yellow needles, m.p. 95.0° C.

*Reaction with methyl iodide.*—30 mg. C<sub>5</sub>H<sub>6</sub>S<sub>3</sub> in 20 cc. 50% methyl iodide in ethanol turned red-brown in 40 minutes. No free iodine was present. On chilling to –78° C a red-brown precipitate was obtained. The brick-colored compound (mp., 150.5–151° C) had 40.4% I, 31.28% S; calculated for C<sub>5</sub>H<sub>6</sub>S<sub>3</sub>·CH<sub>3</sub>I, 41.8% I, 31.98% S.

*Reaction with methyl iodide-mercuric iodide.*—30 mg. C<sub>5</sub>H<sub>6</sub>S<sub>3</sub> in 20 cc. 50% methyl iodide-ethanol with 0.5 gram HgI<sub>2</sub> reacted in 4 minutes to give a white-yellow precipitate. After cooling to –20° C this was filtered off. The yellow compound (m.p., 131.0–131.2° C) had 50.6% I, 11.94% S; calculated for C<sub>5</sub>H<sub>6</sub>S<sub>3</sub>·CH<sub>3</sub>I·HgI<sub>2</sub>, 50.2% I, 12.65% S.

*Reaction with mercuric iodide.*—50 mg.  $C_5H_6S_3$  in 5 cc. ethanol was added to 12 cc. ethanol saturated with 2%  $HgI_2$ . A yellow precipitate was obtained immediately. This was filtered, washed with alcohol, and dried. It melted sharply at  $192.5^\circ C$  if put in the bath at  $189^\circ C$ . It decomposed on longer heating to a black tar. It had 40.4% I and 15.1% S; calculated for  $C_5H_6S_3 \cdot HgI_2$ , 41.2% I and 15.5% S.

*Reaction with iodine in carbon tetrachloride.*—100 mg.  $C_5H_6S_3$  in 8 cc. carbon tetrachloride was added to 0.314 gram iodine in carbon tetrachloride. Red-brown precipitate appeared in a few minutes. Recrystallization from carbon tetrachloride gives red-brown microscopic needles (m.p.,  $135.2$ – $136^\circ C$ ). Analysis, 69.1% I, 17.9% S; calculated for  $C_5H_6S_3 \cdot 3I$ , 70.1% I, 17.7% S.

*Reaction with chlorine and water.*—400 mg.  $C_5H_6S_3$  were suspended in 10 cc. of glacial acetic acid to which 3 cc. of water were added<sup>8</sup>. Chlorine gas was passed through the suspension kept at  $10^\circ C$  until the solid disappeared. If the chlorine is passed in slowly the solution turns yellow, orange, red, then black, then quickly fades to a light yellow, all in a few moments.

The ether extract of the reaction mixture on occasion gave square plates soluble in alcohol, insoluble in water, m.p.  $76$ – $82^\circ C$ , 49.7% Cl. More often no crystals appeared here.

The product from the water-acid solution was odorless. The two fractions, ether-soluble and water-soluble, were combined, taken up in ether, and added to an ether solution of *p*-toluidine. A white precipitate immediately fell out. On recrystallization from ethanol-water it had a melting point of  $221^\circ C$  (turned yellow at  $214^\circ C$ ), 8.03% N, 10.3% S, 54.0% C, 6.45% H. Calculated for *p*-toluidine sulfate  $[(CH_3C_6H_4NH_2)_2 \cdot H_2SO_4]$ , 8.9% N, 10.2% S, 53.8% C, 6.4% H.

*Reaction with Raney nickel.*—Hydrogenation using the adsorbed hydrogen in Raney nickel was attempted according to the method of Mzingo and co-workers<sup>9</sup>. Appreciable sulfur was removed this way, as shown by analyses of the nickel catalyst. Unfortunately only a few milligrams of this material were forthcoming; consequently no further information could be obtained.

*Reaction with copper or silver powder.*—No desulfurization could be observed on refluxing copper or silver powder with  $C_5H_6S_3$  in *n*-heptane.

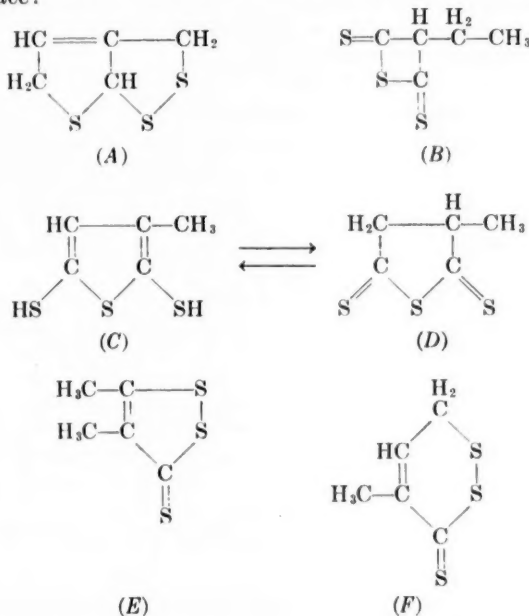
*Reaction with Grote's reagent.*—Grote's reagent<sup>10</sup>, a specially selective nitroprusside reagent for the thiol group, gave a positive red-purple test with  $C_5H_6S_3$ . This reagent was tested on several of the usual sulfur-containing rubber accelerators with the following result: Negative result (green coloration): 2-mercaptobenzothiazole, benzothiazoyl disulfide, and piperidinium pentamethylenedithiocarbamate. Negative result (yellow coloration): trithiane, tetramethylthiuram disulfide, tetramethylthiuram monosulfide, *n*-propyl sulfide-*n*-propyl disulfide, and run 7, fraction 4 (a pentasulfide). Positive result (red-purple): thioglycolic acid (transitory), amyl mercaptan, and *tert*-amyl mercaptan. These last two gave a green color until reduced with potassium cyanide, whereupon they gave the usual red-purple.

*Reaction with alkali.*—Alcoholic potassium hydroxide added to  $C_5H_6S_3$  in ethanol turned blue-red in 5 minutes. On addition of hydrochloric acid the color faded but was brought back by addition of alkali. Huppert<sup>11</sup> described a similar color change using the reaction product of sulfur and isophorone.

*Reaction with sodium ethylate and potassium sulfide.*—On treating  $C_5H_6S_3$  in ethanol with either sodium ethylate or potassium sulfide-potassium hydroxide solution<sup>12</sup>, a red-blue water-soluble compound was formed that could not be separated from the salts present.



The empirical formula,  $C_5H_6S_3$ , and the molecular weight, 172, allow any of the following structures for this compound. These structures all have the 2-methyl-2-butene carbon skeleton, since it is unlikely that at  $140^\circ C$  any carbon bonds should be broken and since no isomerization of the unreacted olefin takes place:



After this article had been submitted for publication, the unpublished work of Bottcher and coworkers<sup>13</sup> in Germany became available. This series of three papers discussed in detail many compounds of the type  $C_5H_6S_3$ , which were named trithiones. The general structure *E*, where the methyl groups can be replaced by any hydrocarbon radical or hydrogen, was assigned on the basis of seven reactions.  $C_5H_6S_3$  was prepared from isoprene and sulfur in 5 per cent yield. According to Bottcher's own work, his structures *E* and *F* do not account for the addition of methyl iodide, which ordinarily splits a disulfide linkage. The oxidative splitting off of two sulfur atoms by hydrogen peroxide, which usually attacks  $C=S$  groups, is also not accounted for by either structure *E* or *F*. The structures *B* or *D* would satisfy these requirements.

The authors feel that the thione-thiol tautomerism displayed by compounds *C* and *D* accounts for most of the reactions observed. This structure was suggested for the colored compound 2,6-dithioketo-3,5-dimethyl-1-thio-4-pyranone by Schonberg and Asker<sup>14</sup>. However, reaction of this compound with methyl iodide apparently does not follow the same course as does  $C_5H_6S_3$ .

Structures *C* and *D* are felt to represent  $C_5H_6S_3$  best for the following additional reasons. The methyl iodide reaction shows presence of a single sulfide sulfur not alpha to a double bond. This favors structures *B*, *C*, or *D*. The methyl iodide-mercuric iodide reaction shows the absence of disulfide or polysulfide sulfur. This again favors *B*, *C*, or *D*. Oxidation with chlorine removed all the sulfur. This would favor structures *B*, *C*, or *D*. Grote's reagent gives a positive test for mercaptan group. This would favor structures *C* and

*D* over structure *B*, since the formation of a thiol structure from *B* leads to a sulfur bond on a carbon alpha to a double bond.

#### DATA SUMMARY

From the data given the following can be set forth concerning the reaction of 2-methyl-2-butene with sulfur at 141.6° C.

The color changes with reaction time, yellow to orange to red to black, parallel those of rubber-sulfur stocks.

Sulfur combination rate is directly proportional to reaction time as in rubber-sulfur vulcanization (Figure 1).

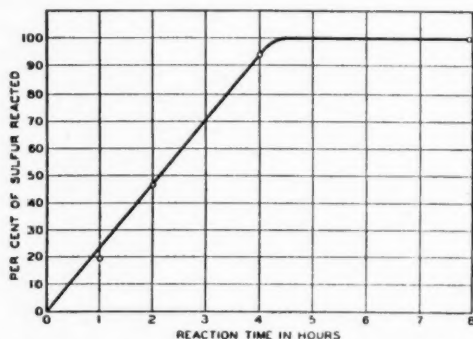


FIG. 1.—Effect of time on sulfur reacted. Reaction of 2-methyl-2-butene with 7.4% sulfur at 141° C.

The absolute reaction rate of 2-methyl-2-butene with sulfur is twice that of pale crepe rubber with sulfur.

Olefin combination rate is nearly proportional to time until the sulfur is completely combined, whereupon a further slow reaction takes place (Figure 2).

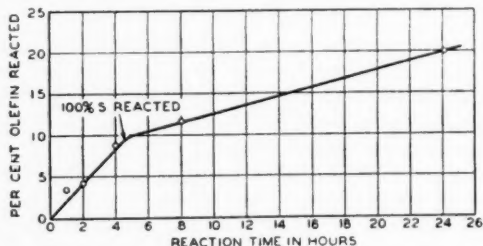


FIG. 2.—Effect of time on olefin reacted. Reaction of 2-methyl-2-butene with 7.4% sulfur at 141° C.

Starting with equal mole quantities of olefin and sulfur there is considerable unreacted olefin in the system when 100 per cent of the sulfur has reacted.

Hydrogen transfer takes place resulting in what appear to be hydrogen-rich liquid products and small quantities of solid hydrogen-poor products.

The apparently hydrogen-rich compounds are polysulfides  $R-S_x-R'$ , where  $x$  varies from 2 to 6 and either  $R$  or  $R'$  or both may be alkyl or alkenyl.

The hydrogen-poor compounds are solids, two of which,  $C_5H_6S_3$  and  $C_{10}H_{10}S_3(?)$ , have been isolated. A cyclic acid anhydride in the sulfur system

with thione-thiol tautomerism has been proposed for the structure of  $C_6H_6S_3$ —that is, 2,5-dithione-3 methyltetrahydrothiophene.

Increased reaction time lowers the average value of  $x$  in the polysulfide products  $R-S_x-R'$ .

The higher the value of  $x$  in the polysulfide formula  $R-S_x-R'$ , the more hydrogen above the level  $H_{20}$  is present.

#### REACTION MECHANISM

The mechanism of the initial attack of sulfur in the form  $S_8$  on the olefin is still unknown. In any case, the products which can be isolated from the short-term reaction are polysulfides, where the residues are saturated, unsaturated, or mixtures, but where the largest fraction is probably alkyl-alkenyl.

The hydrogen-poor compounds can result from the initial attack of sulfur on the olefin or from degradation reactions of the polysulfides on long-time heating.

There is another type of hydrogen-poor compound in the residue from molecular distillation. This is indicated by the higher carbon-hydrogen ratio of the residue in run 6 (Table II). Unfortunately the residues of other runs were not analyzed because of the small quantities involved and the difficulty of removing them from the molecular still. The removal involves the use of solvents and evaporation, which, as shown in the analysis, resulted in oxidation.

The viewpoint that studying model system 2-methyl-2-butene-sulfur will give results which can be applied to the rubber-sulfur system is strengthened by the linear nature of the reaction-time curve (Figure 1). In both cases the combination of sulfur varies directly with time. This similarity in kinetics certainly indicates that the mechanisms operating in the two cases are closely related.

The overall reaction of methyl iodide on run 3 polysulfides (Table III) closely resembles that on the 100-rubber-8-sulfur stock SB1A described in a previous paper<sup>3</sup>. At 24° C half of the combined sulfur of this vulcanizate was removed. About the same percentage of the total sulfur-olefin reaction product gave large quantities of trimethylsulfonium iodide. The heavier polysulfides did not split out the latter compound, because at least one sulfur link was on a saturated hydrocarbon group. The sulfur that cannot be removed with methyl iodide at room temperature may be of two types. Either the sulfur is attached to saturated groups or it is in heterocyclic thiophenelike rings. The former reacts when the temperature is raised, whereas the latter is stable to methyl iodide even at elevated temperature. On overcure the polysulfide sulfur reacts further both with double bonds and alpha carbon atoms. This is shown by the further slow reaction of the olefin after all the sulfur is combined (Figure 2).

There remains the reconciliation of the polysulfide formation observed in the 2-methyl-2-butene sulfur reactions with the generally accepted 32 per cent combined sulfur limit in hard rubber.

#### EXPERIMENTAL DETAILS

**2-Methyl-2-butene.**—Cramer<sup>15</sup> disclosed a simplified way of preparing substantially pure olefin. He claims that by use of 48 per cent sulfuric acid, *tert*-amyl alcohol can be selectively dehydrated in a mixture of other amyl alcohols to give a mixture of pure 2-methyl-1-butene and 2-methyl-2-butene. To check this, dehydration of practical *tert*-amyl alcohol was carried out, using

equal volumes of practical *tert*-amyl alcohol and 48 per cent acid at 80° C. The olefins up to 40° C were distilled off and fractionated in an eighty-plate column. Satisfactory 2-methyl-2-butene was produced in this way, although less 2-methyl-1-butene results than from use of pure *tert*-amyl alcohol. This method is much to be preferred, as it eliminates the tedious purification of *tert*-amyl alcohol. The 2-methyl-2-butene had a boiling point at 760 mm. of 38.5° C;  $n_D^{20}$  1.3843; freezing point, -133.6° C. These properties check those in the literature<sup>16</sup>.

The purified olefin was collected during fractionation at -70° and stored at 0° C in Pyrex bottles for 2 weeks in darkness. Then it was rebottled in 500-cc. Pyrex ampoules which were frozen in liquid nitrogen, evacuated, and sealed. The glass-sealed evacuated ampoules of olefin were kept at room temperature in the dark until used. This storage period in some cases was 18 months.

**Sulfur.**—This material, purified by the method of Bacon and Fanelli<sup>17</sup>, was kindly supplied by Rocco Fanelli of The Texas Gulf Sulfur Company. The sulfur was powdered and stored in a desiccator over barium oxide.

**Molecular still.**—A small molecular still was constructed according to a design given by Riegel, Beiswanger, and Lanzl<sup>18</sup>. This still was unsatisfactory for collecting small fractions.

The still of Hickman and Sanford<sup>19</sup> was modified so that fractions of a few drops could be collected and the heating bath precisely controlled. The final design shown in Figure 3 was quite satisfactory. The capacity is 40 cc.

**Procedure.**—The glass reaction bulb was dried by evacuation for 1 hour and then filled with a weighed amount of sulfur and the contents of one 125-cc. ampoule of olefin added. The flask was then sealed off as described for pressure bulbs in the preceding article<sup>3</sup>; this ensured removal of oxygen. The olefin weight was obtained by weighing the sealed bulb and sealed-off tip to 0.01 gram.

After weighing, the bulb was fastened in a special holder and placed in the heavy wire-mesh can. The can with the sealed bulb was placed in the shaker and immersed in the hot oil bath. The shaking rate was 4 cycles per second. A Micromax recorder-controller gave continuous temperature readings to  $\pm 0.2^\circ$  C. The reaction time was taken from the moment of immersion to that of removal from the bath in analogy to rubber molding practice.

The bulb was allowed to cool to room temperature; it was then placed in the refrigerator at 0° C for 48 hours. The bulb was then cooled to -78° C for at least 1 day before it was opened at room temperature. The liquid product was decanted into a weighed, pear-shaped distilling flask. The solid in the bomb was washed quickly with petroleum ether at -20° C and weighed. The petroleum ether wash was evaporated and the residue weighed and discarded if it was sulfur.

The liquid product was immediately stripped of its unreacted olefin by fractional distillation at a nitrogen pressure of 215 mm. of mercury; at this pressure 2-methyl-2-butene boils at 8° C with a pot temperature of only 22° C. Any attempt to distill off the olefin at atmospheric pressure seriously changes the sulfur reaction products which turn back. The stripped sulfur-olefin liquid products were stored at 0° C under nitrogen until they were molecularly distilled.

The molecular distillation was carried out at as low a temperature as possible and at as high a vacuum as the mercury diffusion pump produced. Here also any overheating resulted in change of the product color and character.

The condenser was kept at  $-78^{\circ}\text{C}$  with dry ice and acetone. Fractions were taken on the basis of all the material which came over at a given temperature starting at  $25^{\circ}\text{C}$  and slowly rising to  $140^{\circ}\text{C}$  with pauses at  $30^{\circ}$ ,  $40^{\circ}$ ,  $60^{\circ}$ ,  $90^{\circ}$ , and  $140^{\circ}\text{C}$ . The products were weighed and kept at  $0^{\circ}\text{C}$  under nitrogen. In certain experiments solids were obtained on the condenser during the dis-

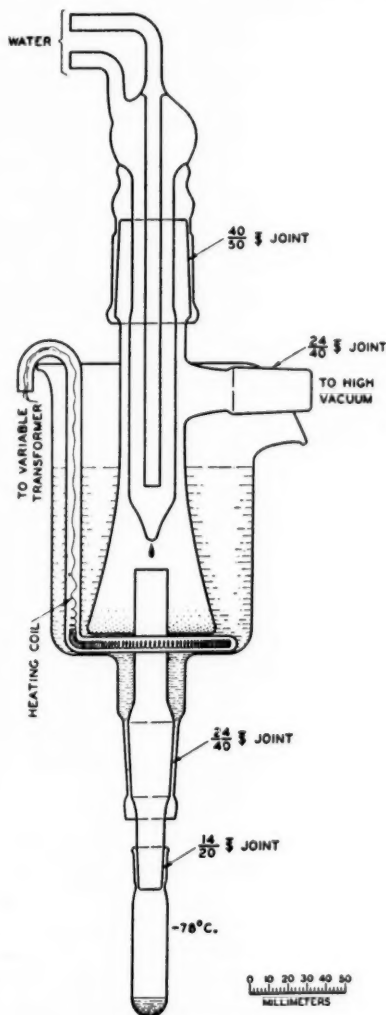


FIG. 3.—Improved simple molecular still.

tillation. In this case the still was dismantled to remove the solid, reassembled, and the distillation resumed. The still was always cooled to room temperature before opening to air. When the solid reaction residue was not sulfur, it was sublimed in the molecular still. In this case the product was a solid adhering to the condenser.

Cryoscopic molecular weights were obtained using benzene. Melting points are the corrected values.

*Refractive index.*—The refractive index of the liquid products was determined in a Pulfrich refractometer. The index of the liquid polysulfides changed very rapidly on exposure to air, a change of 0.003 in 2 hours was common.

#### ACKNOWLEDGMENT

The analytical data presented here are the work of Doris C. Tranberg and the late F. C. Koch. Special glassware was fabricated by G. P. Spindler.

#### REFERENCES

- <sup>1</sup> Midgley, Henne and Sheppard, *J. Am. Chem. Soc.* **54**, 2953 (1932); **56**, 1326 (1934); *RUBBER CHEM. TECH.* **5**, 530 (1932); **7**, 520 (1934).
- <sup>2</sup> Meyer and Hohenemser, *Helv. Chim. Acta* **18**, 1061 (1935); *RUBBER CHEM. TECH.* **9**, 201 (1936).
- <sup>3</sup> Selker and Kemp, *Ind. Eng. Chem.* **36**, 16 (1944); *RUBBER CHEM. TECH.* **17**, 303 (1944).
- <sup>4</sup> Friedmann, *Ber.* **49**, 1344, 1551 (1916); *Petroleum-Z.* **11**, 693 (1916).
- <sup>5</sup> Schwarzkopf, *Bull. soc. chim., Mem.* [5] **2**, 64 (1935); *RUBBER CHEM. TECH.* **8**, 225 (1935).
- <sup>6</sup> Armstrong, Little and Doak, *Ind. Eng. Chem.* **36**, 628 (1944); *RUBBER CHEM. TECH.* **17**, 788 (1944).
- <sup>7</sup> Barbaglia, *Ber.* **13**, 1574 (1880); **17**, 2654 (1884).
- <sup>8</sup> Douglass and Johnson, *J. Am. Chem. Soc.* **60**, 1486 (1938); Lee and Dougherty, *J. Org. Chem.* **5**, 81 (1940).
- <sup>9</sup> Mozingo, Wolf, Harris and Folkers, *J. Am. Chem. Soc.* **65**, 1013 (1943); Snyder and Cannon, *J. Am. Chem. Soc.* **66**, 155 (1944).
- <sup>10</sup> Grote, *J. Biol. Chem.* **93**, 25 (1931).
- <sup>11</sup> Huppert, U. S. patent 2,397,355 (Mar. 26, 1946).
- <sup>12</sup> Dutcher, Johnson and Bruce, *J. Am. Chem. Soc.* **60**, 1486 (1938).
- <sup>13</sup> Botcher and Luttringhaus, Office Pub. Board, Rept. **1707** (1944).
- <sup>14</sup> Schonberg and Asker, *J. Chem. Soc.* **1945**, p. 198.
- <sup>15</sup> Cramer, U. S. patent 2,299,801 (Oct. 27, 1942).
- <sup>16</sup> Am. Petroleum Inst. Research Project No. **44** at Natl. Bureau of Standards, "Selected Values of Properties of Hydrocarbons", Table 8a, Part 1 (June 30, 1945).
- <sup>17</sup> Bacon and Fanelli, *Ind. Eng. Chem.* **34**, 1043 (1942).
- <sup>18</sup> Riegel, Beiswanger and Lanzl, *Ind. Eng. Chem. Anal. Ed.* **15**, 421 (1943).
- <sup>19</sup> Hickman and Sanford, *J. Phys. Chem.* **34**, 637 (1930).



# CERTAIN FUNDAMENTAL CONCEPTS RELATING TO NONPOLAR MECHANISMS IN OLEFINIC SYSTEMS \*

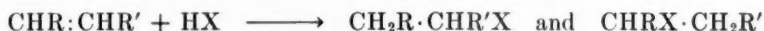
E. H. FARMER

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, WELWYN GARDEN CITY, HERTS, ENGLAND

Extensive investigation of four important and superficially dissimilar types of reactivity which are observable with olefinic hydrocarbons has left little doubt as to the facility with which nonpolar types of reaction can occur, and has revealed what appears to be a general rule governing nonpolar additive reactivity—a rule distinct from, and indeed the counterpart of, that governing ionic or polar additivity. By application of this rule it is possible to formulate the purely additive lines of reaction which can occur between olefinic substances and appropriate reagents, but the actual courses pursued are largely determined by dual factors of hydrogen-lability and additive capacity on the part of the olefin and by the chemical character on the part of the reagent. The present object is to outline a coherent hypothetical way of viewing the diverse and somewhat complicated phenomena which result from the interaction of the various classes of olefins with the reagents in question, the latter being substances such as oxygen, sulfur and maleic compounds, which can be regarded as bi-functional reagents possessing easily evoked free-radical combining characteristics.

## OLEFINIC ACTIVITY

*The Markovnikov and the radical-addition rules.*—It is convenient first to consider for purposes of contrast and differentiation the salient features of polar addition to olefinic systems. A polar reagent of the type  $HX$ , where  $X$  is anionic (e.g.  $Cl$ ,  $I$ ,  $SO_3H$ ) adds to the ethylenic bond of a simple olefin,  $R \cdot CH:CHR'$ , in either direction and to comparable extents provided that the groups  $R$  and  $R'$  are not polarly very dissimilar, e.g.:



As soon, however, as the olefinic system in ethylene is rendered unsymmetrical about the double bond by alkyl substitution of one, two, or three hydrogen atoms, the direction of addition of the reagent becomes precisely determined and can be described in terms of the well known Markovnikov rule. Addition, therefore, to a system,  $R \cdot CH:CH_2$ ,  $RR'C:CH_2$ , or  $RR'C:CHR''$ , proceeds in such a way that the hydrogen ion of the reagent (or in the initiatory stage often hydron derived from a catalyst) adds to the more hydrogenated ethylenic carbon atom and the anionic component of the reagent to the less hydrogenated one, e.g.:



Recent results in the organic field lead, both on experimental grounds and as a matter of logical necessity, to the conclusion that the addition of a polar reagent

\* Reprinted from the *Journal of the Society of Chemical Industry*, Vol. 66, No. 3, pages 86-93, March 1947.

HX to the unsymmetrical alkylethylenes in question occurs exclusively in the direction laid down by the Markovnikov rule and not merely predominantly.

When one turns to nonpolar (radical) reactions, however, ethylenic additivity is only one of two distinct courses which organic reactivity can follow. The reagent may, instead of adding to the double bond, combine with the olefin by replacing one of the  $\alpha$ -methylenic hydrogen atoms. The additive reactivity will be considered first. The first precise ideas regarding the ability of a reagent containing active radical centers (hereafter called a radical reagent) to add to an olefinic bond arose in connection with the peculiar ability of hydrogen bromide to add to an unsymmetrical alkylethylene in both of the possible directions if the olefin was contaminated by traces of peroxide or exposed to oxygen, but only in the normal direction as required by the Markovnikov rule if it were free from these contaminants. The abnormal direction of addition, which could be made to replace wholly the normal direction, was proved to be due entirely to the presence of the contaminants<sup>1</sup>, and the most acceptable hypothesis to explain the reversal of the additive direction which set in where a peroxidic contaminant was present involved the idea that hydrogen bromide reacted in these abnormal additions not as a polarized reagent  $H^+Br^-$ , the hydrogen ion of which initiated reaction by adding to the more hydrogenated of the ethylenic carbon atoms, but as a neutrally-dissociated reagent, the nonpolar (radical) bromine atom of which initiated the attack on the ethylenic bond. Clearly if there is to be a fundamental and rigidly observed distinction between the normal and abnormal types of additive reaction, the two being correlated respectively with tendencies to polar and nonpolar mechanisms of reaction, the latter of these must logically be regarded (as by definition) to involve not merely the initiation of reaction by a radical reagent (atom or molecule) but also exclusive initiation in this way. Furthermore so far as addition to an unsymmetrical alkylethylene is of free radical or abnormal type, the radical component initiating the reaction must add exclusively to the more hydrogenated of the ethylenic carbon atoms. This requirement constitutes the *radical-addition rule*, which stands as the counterpart of the Markovnikov rule applicable to polar additions. Thus in the olefinic systems,  $CHR:CH_2$ ,  $CRR':CH_2$  and  $CRR':CHR''$ , nonpolar addition by a reagent HX will give, respectively, and invariably, first:  $CHR \cdot CH_2X$ ,  $CRR' \cdot CH_2X$

and  $CRR' \cdot CHR''X$ , leaving the less hydrogenated ethylenic carbon atom in

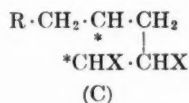
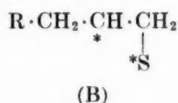
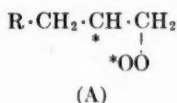
each system in an unstable neutral (radical) condition, and, hence, under the necessity to seek stabilization in one of several recognized ways, e.g., by uniting with a radical center in another atom or molecule, by extracting a neutral hydrogen atom from a colliding reactant (usually an olefin molecule) or from the surroundings, or by facilitating the shedding of a hydrogen atom from a carbon atom adjacent to the radical center to form a double bond. The important concept in the abnormal additive scheme is that a radical entity (any radical entity, of suitable stability which may be available in the reactant system) can, in general, add to the appropriate end of an ethylenic double bond as laid down in the radical-addition rule, unless steric hindrance prevents; and subsequently the radical-adduct thus formed becomes stabilized, which, as experience shows, happens most often in nonpolymeric processes by the gain or loss of a neutral hydrogen atom.

Now among common substances which are known to react with olefins and also to possess or to be capable of manifesting radical characteristics are the

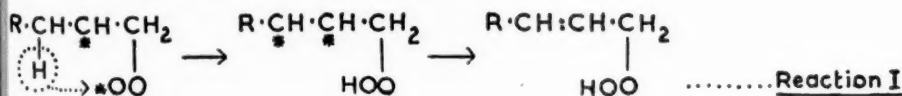
paramagnetic elements oxygen and sulfur, whose molecules possess unpaired electrons, and also most olefins, since their molecules when thermally or photochemically energized appear to be capable of assuming active forms which embody, or easily pass into, biradical forms  $>\text{C}-\text{C}<.$  The outcome of reac-

tion between oxygen and olefins is now very largely known in a qualitative sense, the usual and the most abundant products being simple hydroperoxido-derivatives of the olefins, in which each  $\cdot\text{OOH}$  group is situated on an  $\alpha$ -methylene C—H bond (*e.g.*,  $>\text{C}-\text{H} + \text{O}_2 \longrightarrow >\text{C}^* + \cdot\text{OOH}$ ), the position of the double bond remaining unchanged, and (2) by addition of oxygen at one end (the appropriate end) of the double bond. Now it has become very clear from qualitative and kinetic observations that effective reaction in the case of the most reactive group of unconjugated olefins (comprising compounds containing the  $\Delta^{1,4}$  system,  $\text{CH}:\text{CH}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}\cdot$ ) proceeds by scission of the reactive C—H bond, being in fact propagated by a chain mechanism<sup>2</sup>; initiation also in this favorable case, probably occurs mainly in exactly the same way, and therefore in minor degree only by double bond addition. Oxygen is known, however, to react very extensively with conjugated compounds and with  $\alpha\alpha$ -diphenylethylene by polymeric addition to the ends of the double bond systems. It seems not unlikely, therefore, that for all olefins in which  $\alpha$ -methylene reactivity by organic structural standards is not strongly developed, *e.g.*, normal-chained monoolefins, the tendency to additive initiation of reaction becomes more pronounced<sup>3</sup>, and of course in those olefins which contain no  $\alpha$ -methylene groups must be the sole initiating mechanism. For this reason the ever present possibility of initiation by an additive step has been allowed for in the existing formulation of peroxidation mechanism<sup>4</sup>. Hence it is of some interest to consider specifically and in the light of the radical-addition rule the exercise of the additive function (as the complement of the  $\alpha$ -methylene substitutive function) over a short series of potentially radical reagents.

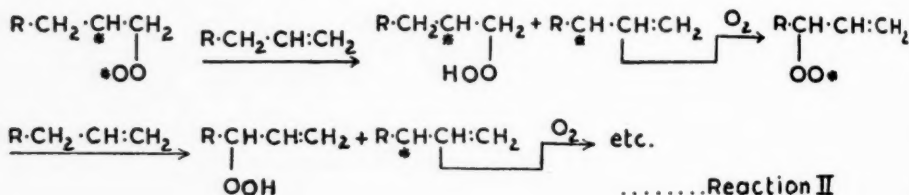
The system,  $\text{R}\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , may be taken as representative of all unsymmetrical ethylenes belonging to the three types  $\text{CHR}:\text{CH}_2$ ,  $\text{CRR}':\text{CH}_2$ , and  $\text{CRR}':\text{CHR}''$ ; the addition thereto of oxygen or sulfur, or of an olefinic reagent,  $\text{CHX}:\text{CHX}$ , may be expected, if it occurs at all, to be initiated uniquely (each to each) by the steps (A), (B) and (C):



Since in the subsequent stabilization of these radical intermediates the availability of hydrogen atoms will be a primary concern, the outcome of the initiating steps can hardly avoid being considerably influenced by the hydrogen lability (that is to say, by the ease of severing apolarly the  $\alpha$ -methylene C—H bond) of the olefin employed, as well as by the chemical character of the addendum molecule. In those olefins whose  $\alpha$ -methylene hydrogen lability is low the subsequent stabilizing reaction may well be confined to a simple intramolecular transfer of hydrogen, thus,



the detachment of hydrogen from the former  $\alpha$ -methylene group being greatly assisted by the radical center now adjoining it. Two necessary results of the intramolecular mechanism are (1) that hydroperoxidation is accompanied by double bond displacement, and (2) that the reaction following the initiating stage (A) is not propagated by a chain reaction. In those olefins, however, which are characterized by high hydrogen lability, the reaction is likely to be, and is known actually to be, propagated by chain reactions, because then the hydrogen atom required for stabilization of the peroxide group in the initiating form (A) can with advantage be derived from the  $\alpha$ -methylene group of an external olefin molecule. Thus we get the sequence:

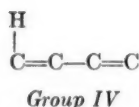
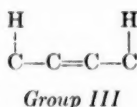
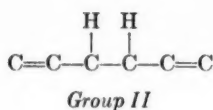
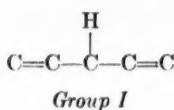


In this case the ultimate fate of the particular molecules which initiate peroxidative reaction is of but slight importance (because they will be relatively few), provided the reaction chains are reasonably long.

It might be supposed at first sight that the two mechanisms of reaction involving respectively intra- and intermolecular hydrogen transference ought to be distinguishable by qualitative experimental methods, owing to the structural difference between the peroxides formed in Reactions I and II, but such discrimination may be hindered by the resonance which is always potential in the three-carbon radical system  $\cdot \overset{*}{\text{C}} \cdot \overset{*}{\text{C}} \cdot \overset{*}{\text{C}} \cdot (\cdot \overset{*}{\text{C}} \cdot \overset{*}{\text{C}} \cdot \text{C} \rightleftharpoons \cdot \overset{*}{\text{C}} \cdot \overset{*}{\text{C}} \cdot \overset{*}{\text{C}} \cdot)$ , since this implies that the ultimate position of the double bond in the reaction product is determined by the relative stabilities of the resonance hybrids, so that, in the hydroperoxidation (for example) of  $\cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot$  by the intermolecular process, either or both of the peroxide-forms  $\cdot \text{CH}(\text{OOH}) \cdot \text{CMe} \cdot \text{CH} \cdot$  and  $\cdot \text{CH} \cdot \text{CMe} \cdot \text{CH}(\text{OOH}) \cdot$  might turn up. Hence kinetic measurements may be required to discriminate conclusively between the two mechanisms.

#### UNSATURATION PATTERN AND HYDROGEN LABILITY

Olefinic systems may be arranged in four groups according to hydrogen lability, the latter being determined largely by the unsaturation pattern, but partly by the presence or absence of ethylenic substitution on the ethylenic carbon atoms. Olefins in which consecutive double bonds are separated by a single methylene group, *i.e.* unspaced or  $\Delta^{1,4}$ ,  $\Delta^{1,4,7}$ , etc., olefins (Group I), show the highest degree of hydrogen lability, owing to the central or reactive  $\alpha$ -methylene group being flanked on either side by a double bond. Bi-spaced or  $\Delta^{1,5}$ ,  $\Delta^{1,5,9}$ , etc., olefins (Group II) show a lesser lability, since then each  $\alpha$ -methylene group standing between a pair of double bonds is strongly influenced by the adjacent double bond and less strongly by the more remote one. Mono-olefins (Group III) show a still smaller hydrogen lability, while from conjugated olefins (Group IV) most of the  $\alpha$ -methylenic



hydrogen lability (but not necessarily all, except in members containing no  $\alpha$ -methylene group) appears to be lost. There is, however, a possible important auxiliary to the unsaturation pattern in determining the degree of hydrogen lability which an olefinic system exhibits, and that is alkyl substitution (other substitution is not considered here) at the ethylenic carbon atoms. No experimental observations have yet been made with alkyl derivatives of the unspaced olefins belonging to Group I, such as  $\text{CH}_2:\text{CH}\cdot\text{CH}_2\cdot\text{CMe}:\text{CH}_2$ , but general experience with the large group of short- and long-chain polyisoprenes belonging to Group II points to a definite facilitating influence which the methyl group in each isoprene unit,  $\cdot\text{CH}[\text{H}]\cdot\text{CMe}:\text{CH}\cdot\text{CH}_2\cdot$ , exerts on the detachment of hydrogen from the immediately adjoining  $\alpha$ -methylene group. Some caution, however, is necessary here, because kinetic evidence bearing on the point is entirely lacking. The speed of radical reaction, nevertheless, appears in general to be considerably increased for such unsymmetrically alkylated olefins (doubtless in conformity with the unidirectional orientation of hyperconjugation within the system,  $\cdot\text{CH}_2\cdot\text{CR}:\text{CH}\cdot$ ), but this increase may perhaps depend in part on the additive functioning of the double bond, and to this extent be connected with the strictly one-way (instead of two-way) capacity for a radical to add to the ethylenic center: experimentation has not yet shown to what extent, if any, the reactivity which is enhanced is of purely additive type, i.e., according to Equation I. In the case of olefins of Group IV, hydrogen lability is always likely to be low, owing to the strength of the  $:\text{C}-\text{H}$  bond, but aryl substitution at one end of the diene system sometimes appears (delusively) to facilitate hydrogen-detachment at the opposite end, as in  $\text{CHPh}:\text{CH}\cdot\text{CH}:\text{CH}[\text{H}]$  or  $\text{CHPh}:\text{CH}[\text{H}]$ .

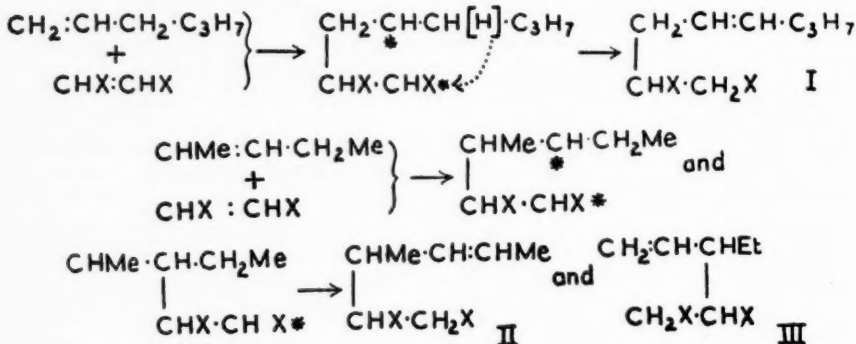
#### INTRA- AND INTERMOLECULAR HYDROGEN TRANSFERENCE

When a radical reaction is propagated by a chain mechanism involving many or few links, the transference of hydrogen required for the addendum to appear at an  $\alpha$ -methylene carbon atom must occur intermolecularly (see Reaction II) because the alternative intramolecular transference inevitably and immediately ends in the production of a nonactivated (nonradical) molecule without affecting external molecules (see Reaction I). If reaction gives in high yield a unimolecular derivative of the olefin such as a hydroperoxide, discrimination between the intra- and intermolecular mechanism, as noted above, can ordinarily only be achieved kinetically. Nevertheless when such reaction occurs in diolefinic systems, a partial discrimination may be possible, since, although the main products for both mechanisms may be the same, certain ones may be different. The state of affairs is best illustrated by the reaction between maleic compounds and olefins of Groups I, II and III.

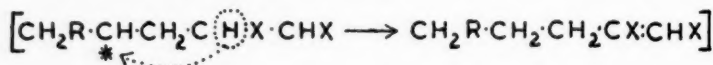


## REACTION OF MALEIC COMPOUNDS WITH OLEFINS

The ease with which thermally promoted reaction occurs between maleic compounds and polyisoprenes or simple olefins has almost from the first been known to be associated with the  $\alpha$ -methylene groups of the olefins<sup>5</sup>, but in the olefins first examined (hydroaromatic compounds) the interrelationship between reaction occurring substitutionally at the  $\alpha$ -methylene groups and additively at the double bonds was obscured by a superimposed and very facile radical reaction, *viz.*, dehydrogenation, and also by the tendency of the maleic compound to undergo self-polymerization<sup>6</sup>. The reaction, however, becomes clarified when open-chain olefins belonging to Groups I-III are examined<sup>6</sup>. Considering the simplest systems first, although that was not the path of experimental development, and adhering rigidly to the radical-addition rule, it may be considered that the energized addendum-molecule—in this case the maleic molecule, which perhaps is to be regarded as a "hot" molecule  $[C=C]^*$ , or alternatively as an already opened-up diradical molecule  $C-C^* \cdot$ , takes the first step<sup>7</sup> by adding to the double bond of the olefin as illustrated above in (C), after which stabilization follows by one of the usual steps enumerated above, but almost entirely by intramolecular hydrogen transference. Thus for 1-hexene, the first end product is in fact (I) and that from 2-pentene (which belongs to the symmetrically substituted group of ethylenes, and hence is not restricted to unidirectional radical addition) is a mixture of (II) and (III):



But since the first products (I), (II) and (III) are all olefinic substances of the types  $\text{CHR}:\text{CH}_2$  and  $\text{CHR}:\text{CHR}'$ , further uni- or bidirectional addition may well take place in exactly the same way as before to give doubtless two mono-olefinic dimaleic adducts from both (I) and (II), unless steric hindrance intervenes, and one from (III)<sup>8</sup>. But although in the intermediate biradical forms the transference of hydrogen from olefin to addendal component is the general rule, it is not perhaps the exclusive rule, for occasional observations have suggested that a small part of some adducts contains a maleic instead of a succinic grouping. Whether hydrogen transference then goes (in part) the reverse way:





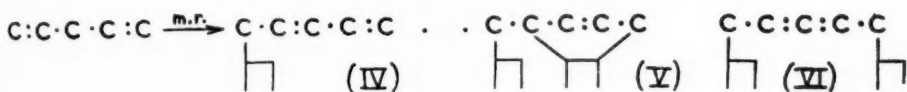
or is achieved intermolecularly is not immediately obvious. The chief conclusion to be drawn, however, is that with fair certainty the reaction begins



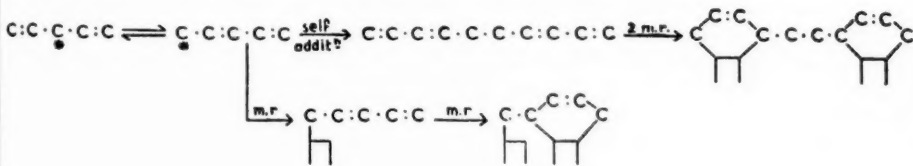
additively, and probably in the main amounts to a simple radical addition. This order of events was not revealed when the symmetrical cyclic olefin cyclohexene or long-chain polyisoprenes were studied; for the  $\alpha$ -methylene hydrogen detachment mechanism necessarily gave exactly the same result in the case of the simple cyclic system as the additive mechanism, owing to the cyclic nature and symmetry of the cyclohexene, and the occurrence of double bond-shift in the polyisoprenic systems was difficult to detect experimentally, owing to the resinous and complicated nature of the products.

When one turns to unspaced polyene systems, the possibilities of reaction become more elastic, for the high lability of the  $\alpha$ -methylenic atoms facilitates intermolecular hydrogen displacement, and in the case of olefin autoxidation leads to reaction-chains of the kind already considered. But in the olefin-maleic reaction, certain adduct-forms are common to the additive and the hydrogen-displacement mechanisms, whereas others will arise by the hydrogen-displacement mechanism only. Thus in the case of  $\Delta^{1,4}$ -pentadiene purely additive reaction would be expected to pursue the following course in which

*m.r.* represents a maleic reagent  $\text{CHX}:\text{CHX}$  and the symbols  and  respectively the succinic groupings  $\cdot\text{CHX}\cdot\text{CH}_2\text{X}$  and  $\cdot\text{CHX}\cdot\text{CHX}\cdot$ :

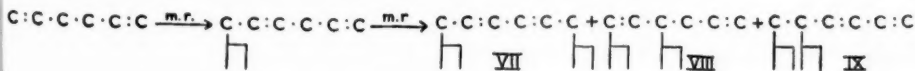


The chief reaction products, even though equimolecular quantities of the reactants are taken in the first place, are then likely to be the dimaleic adduct (V), together with (a probably smaller amount of) the conjugated monomaleic adduct (IV); the allenic dimaleic adduct (VI) could only be formed if additive reaction occurred simultaneously at the two end carbon atoms, and hence probably be present as a minor product. In contrast to this, the course pursued if reaction proceeded by the intermolecular mechanism of hydrogen displacement—following an initiatory step involving addition of the reagent at one end of a double bond—would be likely to be the following:



The actual experimental results obtained strongly favor the latter formulation of the course of reaction.

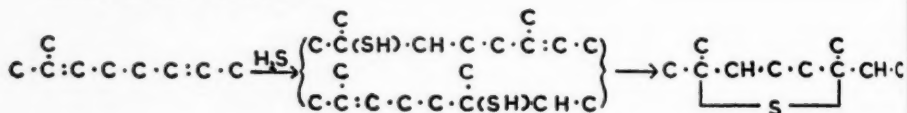
In the case of diallyl, however, where hydrogen lability is bound to be considerably inferior to that characterizing pentadiene, the purely additive type of reaction might well be the dominant, or possibly the almost exclusive one. Then the course of reaction would be expected to be:



The experimental results obtained, to the extent that detailed investigation has yet proceeded, conform with this formulation, but the two conjugated adducts (VII) and (IX) would be formed by either mechanism, and the presence of the unconjugated adduct (VIII) has not been experimentally verified.

#### THE RADICAL MECHANISM OF SULFURATION

*Monosulfuration by hydrogen sulfide (polar and radical).*—It is not surprising that sulfur, belonging to the same chemical group as oxygen, shows strong resemblances to the latter in its reaction with olefins; and in fact the experimental results obtained in the case of monoolefins and bispaced polyolefins fall into line with the concepts described above. When the sulfur is employed in the form of hydrogen sulfide, reaction with olefins proceeds additively, but the addition may be of polar or radical type. Ordinarily the polar addition of hydrogen sulfide occurs with very considerable difficulty, owing to the feeble polar dissociation of the reagent, but the reaction can be accelerated by using a metallic sulfide, or a little free sulfur as catalyst<sup>9</sup>. The product is then invariably formed in strict conformity with the Markovnikov rule<sup>10</sup>. Thus the diisoprene dihydromyrcene gives the two expected thiols and the corresponding cyclic sulfide

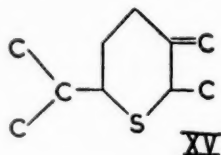
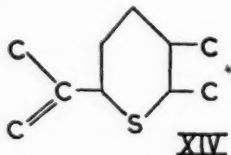
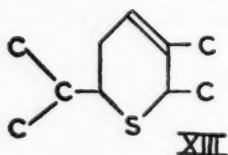


The analogous diolefin geraniolene,  $\text{CMe}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe:CH}_2$ , behaves exactly similarly<sup>11</sup>. If, however, the reaction of hydrogen sulfide with olefins is conducted in ultraviolet light, the reaction can thus proceed exclusively in conformity with the radical-addition rule<sup>6</sup>, the effective reagent being radical sulfur ( $\cdot\text{S}\cdot$ ) or radical thiol ( $\cdot\text{S:H}$ ), as at the top of page 35. It is to be noted that any tendency which might exist for the two mercaptoisomers to cyclize by a polar addition of the  $\cdot\text{SH}$  group to the remaining double bond would be unlikely to succeed, since only a 7-membered ring could be formed. The strange part about these additions is that sulfur, which *a priori* would be expected to, and (in view of the foregoing ultraviolet light reaction) obviously can, function as a radical reagent, is found to be a very effective catalyst for the polar addition of hydrogen sulfide. Presumably the reason must be that the sulfur by coördination on the sulfur atom of the hydrogen sulfide, to give  $\text{H}_2\text{S} \rightarrow \text{S}$ , thereby increases the ionization of the hydrogen sulfide.

*Monosulfuration by sulfur.*—Sulfur, as might be expected from its strong coördinating capacity, tends to react with olefins in straight chains of from one to six sulfur atoms ( $\text{S}_7$ - and  $\text{S}_8$ -chains have not yet been detected), doubtless derived from the thermal scission of original cyclic  $\text{S}_6$ - or  $\text{S}_8$ -forms<sup>12</sup>. The fate of a single sulfur atom acting as reagent may first be considered, and reactivity of this kind is best displayed in relation to an olefinic system which is suitably substituted by alkyl groups (to ensure that differences between the results of radical addition and polar addition, as determined by the operation of their respective additive rules, will be clear cut), it being assumed that sulfur acts uniformly in respect of both of its potential valencies when it functions as a radical reagent. The diisoprene dihydromyrcene, or its close analog<sup>7</sup> geraniolene, admirably serves the purpose.



that the second C—S link is often established in rapid succession to the first (to give XII) before the free end of the first double bond is stabilized<sup>13</sup>. Hence the way in which the diradical represented by (XII) becomes stabilized will probably be variable, although on the average one double bond will be formed and one radical center stabilized by hydrogen capture. This means that both the cyclic sulfides (XIII) and (XIV) may well appear in good yield, and possibly (XV) in slight yield; but also, since the state of unsaturation there dis-



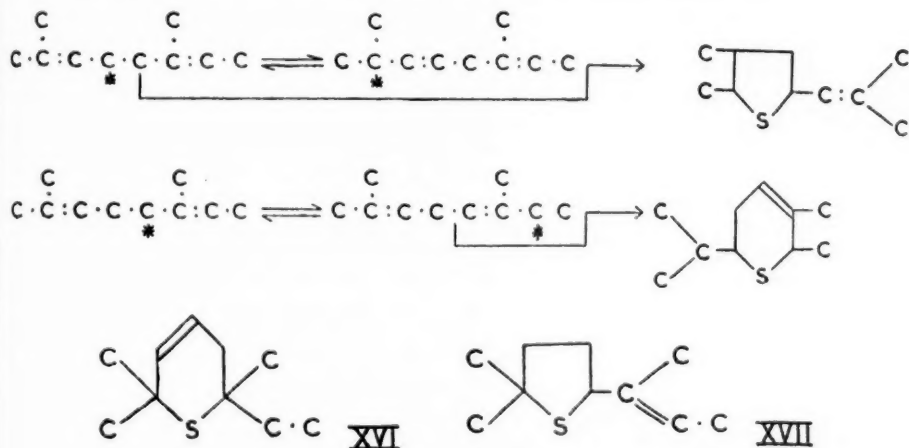
played is really only an average one, there may well be some fully saturated cyclic sulfide and some diolefinic cyclic sulfide—a state of affairs which is definitely found to be realized in the case of the less complex monoolefin sulfur products<sup>12</sup>.

This latter disproportionation effect could not take place without intermolecular hydrogen displacement, and there is ground for believing that the hydrogen atoms of the pairs of methylene groups in polyisoprenes have sufficient lability to facilitate strongly intermolecular hydrogen displacements in general. If such intermolecular displacements take place in appreciable degree, then the first step towards the successful propagation of chain reactions (even though of only a few links) has been taken: in that case a somewhat different structural type of cyclized product must appear, for the union of sulfur will now be promoted at the  $\alpha$ -methylenic carbon atoms, and hence complications due to resonance arise. The two most likely points of attack in the dihydromyrcene molecule are the carbon atoms between the double bonds; and hydrogen displacement from these gives, owing to resonance, four possible radical forms, only two of which could give by combination with a sulfur atom and subsequent cyclization a 5- or 6-membered sulfide ring (see next page).

There are two further possibilities that require consideration, viz., that in so far as any sulfo radical, whether derived by addition of sulfur to a double bond or by direct  $\alpha$ -methylenic attack by the reagent, is unable to stabilize its radical center by adding to a double bond in the same molecule, just because of the unsuitable position of the latter, it may add to the double bond in another olefin molecule, or else acquire a hydrogen atom by collision with another olefin molecule, *i.e.*, by intermolecular transference, and so give a thiol. The first of these contingencies represents the ordinary situation where the hydrocarbon reactant is a monoolefin, and is considered below; the second appears to be of greater importance than might perhaps have been anticipated. If thiol groups are formed extensively from sulfo radicals in the way suggested, many of these are likely to add in polar fashion (as the Markovnikov rule directs) to olefinic double bonds, since the necessary catalyst, sulfur, is available, and new opportunities for forming 5- or 6-membered rings appear with the change to polar addition. These opportunities amount to the production of one 6-membered, and one 5-membered ring, (XVI) and (XVII).

Altogether, then, three principal and one subsidiary 6-membered mono-sulfide rings and two 5-membered rings come into consideration as possible

cyclic sulfo derivatives of dihydromyrcene (or of geraniolene). The cyclic product obtained in practice is demonstrably heterogeneous and its infrared spectrum, as far as its complex character has been interpreted, indicates a preponderance of the structural type shown in (XVI) over that shown in (XIII), and also the presence of some proportion of a compound or compounds containing the grouping  $\text{CH}_2\text{:CRR}'$ , such as (XIV) or (XV). It is interesting that the structural type (XVI) can only arise by a process which involves (1) direct  $\alpha$ -methylenic attack by radical sulfur, and hence intermolecular hydrogen transference, the latter carrying with it the likelihood of a chain mechanism, and (2) the formation by radical mechanism of thiol groups which ultimately become used up by participation in a polar additive reaction. Whether or not 5-membered sulfide rings are present in the diolefin/sulfur product is as yet uncertain; but the complete absence of other than 6-membered cyclic products (thiopyranes) from the diolefin/hydrogen sulfide is firmly established.



*Sulfur as a cross-linking agent.*—It has been noted above that a radical sulfo group attached to an olefinic chain may add to a double bond in another molecule if there is no conveniently situated double bond in the same chain, or simply as the result of propinquity as brought about by the movements of molecules. In the case of a monoolefin, there is no alternative to the intermolecular reaction (unless reaction ends in thiol formation) and this applies both to polar additions of hydrogen sulfide or radical additions of sulfur ( $2\cdot\text{C}:\text{C}\cdot + \text{H}_2\text{S} \rightarrow \cdot\text{CH}\cdot\text{C}\cdot\text{S}\cdot\text{C}\cdot\text{CH}\cdot$ ;  $2\cdot\text{C}:\text{C}\cdot + \text{S} \rightarrow \cdot\text{C}\cdot\text{C}\cdot\text{S}\cdot + \cdot\text{C}:\text{C}\cdot \rightarrow \cdot\text{C}\cdot\text{C}\cdot\text{S}\cdot\text{C}\cdot\text{C}\cdot$ ); but whereas the hydrogen sulfide adducts are saturated monosulfides, the sulfur adducts are unsaturated mono- or polysulfides. Practically the whole of each monoolefin/sulfur reaction product and a large proportion of each polyolefin/sulfur product thus consist of hydrocarbon molecules cross-linked by sulfur, or more explicitly of mono- or polysulfides of the type  $\text{R}\cdot\text{S}_x\cdot\text{R}'$ , where  $\text{S}_x$  consists of a straight chain of from one to (at least) six sulfur atoms and R and R' are on the average, respectively, saturated and monoolefinic. This applies even when only one atomic proportion of sulfur per molecule of olefin is taken (because the sulfur comes to reaction in chains of atoms) and means that, on the average, one of the reacting olefin molecules



gains a hydrogen atom while the other loses one ( $2RH + S_x \rightarrow R \cdot S_x \cdot RH_2$ ). But although  $R_{sat} \cdot S_x \cdot R_{\overline{1}}$  represents the average product from monoolefins, there is always quite a considerable proportion of a mixture (doubtless equimolecular) of  $R_{sat} \cdot S_x \cdot R_{sat}$  and  $R_{\overline{1}} \cdot S_x \cdot R_{\overline{1}}$  as might be expected for a radical reaction:  $C:C + ^*S_x^* \rightarrow C \cdot \dot{C} \cdot S_x^* \xrightarrow{C:C} C \cdot C \cdot S_x \cdot C \cdot C \rightarrow C:C \cdot S_x \cdot C \cdot C$  or  $\frac{1}{2}C \cdot C \cdot S_x \cdot C \cdot C + \frac{1}{2}C:C \cdot S_x \cdot C:C$ . The usual presence of wholly saturated and diolefinic forms mixed with the average forms seems to diminish the possibility that when sulfur adds by one of its valencies to a double bond in one molecule the addition is invariably completed ( $\cdot CH \cdot C:C + S_x \rightarrow \cdot C:C \cdot S_x^* + H^*$ ) before the sulfur adds by its second valency to the double bond of a second molecule. The net result, however, is that, on the average, one of the original two double bonds of the monoolefin molecules is destroyed and one retained, and the original H/C atom ratio of the olefin remains undisturbed in the sulfo product. This result is a general one for unconjugated olefins, including long-chain polyolefins such as rubber<sup>12</sup>; and the cross-linking of separate molecules so achieved appears to be the most important feature in the (unaccelerated) sulfur-vulcanization of rubbers. In the long-chain polyolefinic instances, however, the fact that ordinarily only one or just a few of all the olefinic units present in any molecule become thus linked to an equal number of olefinic units in a second molecule does not destroy the generality of the results regarding the unsaturation and H/C ratios of the sulfo products.

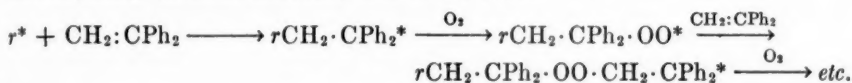
*Controlling factors in cyclization.*—It is convenient at this point to turn aside to consider further the tendency towards cyclization, since this is a matter of great practical importance. The capacity for achievement of cyclization may be regarded as controlled by two factors, *viz.*, (1) by the permissible size of ring, which is affected to some extent by the nature of the atoms taking part, and is the same for polar and radical additions, and (2) by the appropriate additive rule—Markovnikov or radical-addition. Confining attention to the course of radical reactions beginning additively (polar additions vary from these in the obvious way), and dismissing 3-, 4-, and 7-membered rings from consideration as unlikely to be achieved, the application of the second of these factors to the addition of sulfur and maleic compounds, respectively, to substituted and unsubstituted  $\Delta^{1,4}$ - and  $\Delta^{1,5}$ -diolefinic can be represented by the scheme shown opposite.

*The peroxide-catalyzed reaction of maleic compounds.*—The interaction of maleic compounds with olefins and polyolefins can be readily promoted below  $100^\circ$  by the use of peroxides as catalysts, although very substantial amounts of catalyst are required to produce nearly complete maleinization of the olefinic centers, especially in polyolefins<sup>14</sup>. The products on the whole are not very dissimilar from those obtained by thermal promotion, but then exact character is as yet undetermined. Probably the reaction occurs entirely at the  $\alpha$ -methylene groups following hydrogen detachment by  $^*OH$  or other radicals derived from the decomposing peroxide, the radical adducts becoming immediately stabilized, largely by disproportionation.

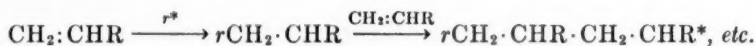
*Polymerization, polymeric peroxidation and autoxidative cross-linking.*—Whenever in a simple olefin there is no  $\alpha$ -methylene group, peroxidation may proceed polymerically, as occurs with  $\alpha\alpha$ -diphenylethylene. Thus reaction may be represented as an interpolymerization of the olefin with unsaturated oxygen, *e.g.*,  $\ddot{O}=\ddot{O}$  or  $\cdot\ddot{O}:\ddot{O}\cdot$ , in which the radical-ended molecule adds to successive monomer molecules in conformity with the radical-addition rule.



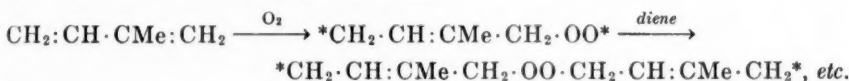
Thus whether reaction is initiated by  $O_2$  or a free radical  $r^*$  derived from a decomposing peroxide molecule, it is of the type:



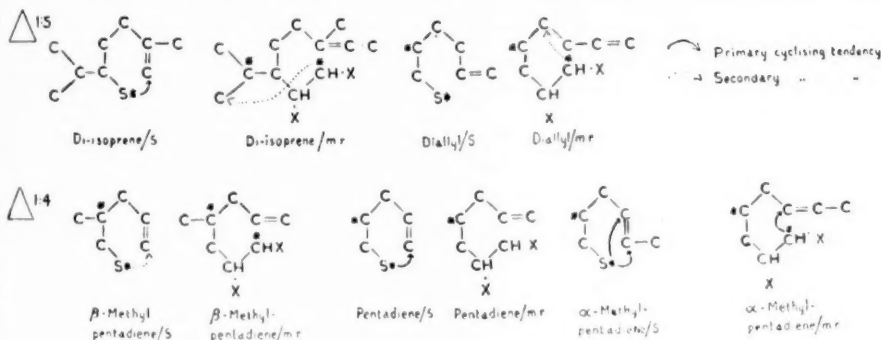
The process is comparable with the nonpolar polymerization of an alkyl-ethylene, which may be formulated as proceeding in conformity with the radical-addition rule after reaction has been initiated by oxygen or a free radical, thus:



A similar representation in conformity with the rule also applies to the polymeric peroxidation of conjugated dienes:



In all these cases terminal  $\cdot OO^*$  groups doubtless become finally stabilized as  $\cdot OOH$  groups, and radical hydrocarbon-ends by gain or loss of hydrogen (dis-



Permissible cyclizations according to the radical-addition rule

proportionation). The counterpart of sulfur cross-linking occurs in some degree with oxygen, for many olefins which give principally hydroperoxides give also some peroxide-linked dimer molecules.

## SUMMARY

The application of polar concepts to the interpretation and systematization of experimental observations in the field of organic chemistry has had such striking success and usefulness during the past twenty-five years that the concepts have become an integral part of organized chemical knowledge. Recent years, however, have seen the steady accumulation of experimental results which do not fit in the polar scheme, and these may be rationally and consistently interpreted as resulting from the occurrence of apolar types of reaction in which the participants are short-lived neutral entities (molecules or atoms) displaying free-radical characteristics. On the apolar basis, the

author outlines a hypothetical correlation of a considerable array of experimental results with which he has been concerned—both as an immediate aid to making sense of what would otherwise seem to be unusually complicated and unintelligible, and with the hope that the views tentatively advanced will furnish suggestive starting points for future kinetic experimentation.

The foregoing account relates to subjects forming part of a program of fundamental research undertaken by the British Rubber Producers' Research Association.

#### REFERENCES

- <sup>1</sup> Kharasch and Mayo, *J. Am. Chem. Soc.* **55**, 2468 (1933); Mayor and Walling, *Chem. Reviews* **27**, 351 (1940).
- <sup>2</sup> Farmer, Bloomfield, Sundralingam and Sutton, *J. Faraday Soc.* **38**, 233 (1942).
- <sup>3</sup> Values of -4 and 14 kcalories have recently been calculated by Bolland and Gee (*J. Faraday Soc.* **38**, 244 (1942)) for the probable heats of reaction due to  $\alpha$ -methylene C—H scission and double-bond addition, respectively, for a  $\Delta^{1,4}$  diene; also corresponding values of 3 and 2 kcalories for a conjugated ( $\Delta^{1,3}$ ) diene, and 7 and 14 kcalories for a moolefin.
- <sup>4</sup> Farmer, "Advances in Colloid Science", New York, **1946**, Vol. 2, p. 312; *J. Faraday Soc.* **42**, 233 (1946).
- <sup>5</sup> Farmer, *J. Faraday Soc.* **38**, 340 (1942).
- <sup>6</sup> Farmer, E. H., and Farmer, M. J., forthcoming papers.
- <sup>7</sup> That the maleic compound takes the first step toward reaction by adding to the olefinic double bond rather than that the olefin first sheds a hydrogen atom under the thermal treatment to produce a reactive radical center is indicated by the facts: (1) that the olefin shows no detectable degree of that isomerization under the thermal treatment, which the onset of any significant degree of thermal hydrogen removal could hardly fail to bring about in virtue of the resonance capacity of the radical propene system; (2) that polymerization also does not occur, although there is evidence that both polymerization and isomerization occur at substantially higher temperatures; and (3) that maleic molecules add very readily to one another at the temperature of the thermal reaction so that there is no hindrance to reaction on the part of the maleic compounds, which itself indicates that a sufficient number of maleic molecules become thermally activated to sustain effective reaction.
- <sup>8</sup> Actually the di- and trimaleic adducts appear to be largely composed of isomers of a different type, formed by a competitive additive reaction. This complicating factor is present throughout the thermally promoted olefin-maleic reactions.
- <sup>9</sup> A good deal of this small amount of sulfur ultimately reacts with the olefins in the characteristic way of sulfur (thus introducing olefinic sulfides as contaminants), but it serves admirably its catalytic purposes.
- <sup>10</sup> Naylor, *J. Polymer Sci.* **1**, 305 (1946).
- <sup>11</sup> The author acknowledges gratefully the invaluable assistance which G. B. B. M. Sutherland and N. Sheppard of Cambridge University have rendered by their investigation by infrared spectroscopic methods of the structures of all the cyclic sulfides herein mentioned.
- <sup>12</sup> Farmer and Shipley, *J. Polymer Sci.* **1**, 293 (1946); Bloomfield, *J. Polymer Sci.* **1**, 312 (1946).
- <sup>13</sup> This would preclude thiol formation through capture by the sulfo radicals of hydrogen atoms from external molecules, and in practice such thiol formation is negligible unless the primary products have been decomposed thermally by incautious treatment during their isolation. It is not impossible, however, that to some extent the cyclic monosulfide is of secondary origin, i.e., is formed by thermal breaking of the sulfur chains in the diolefin polysulfide,  $R-S_x-R$ , previously formed (see below). In any such secondary cyclic product, one C—S link would necessarily be formed and stabilized before the second became a possibility.
- <sup>14</sup> Farmer, *Rubber Tech. Conf. London*, **1938**, p. 256.

# THE ADDITION OF THIOCOMPOUNDS TO OLEFINS.

## I. REACTIONS OF THIOGLYCOLIC ACID, THIOPHENOL, AND ISOPENTANETHIOL \*

J. I. CUNNEEN

BRITISH RUBBER PRODUCERS' RESEARCH ASSOCIATION, 48 TEWIN ROAD,  
WELWYN GARDEN CITY, HERTS, ENGLAND

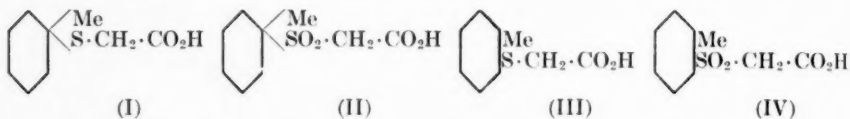
The interaction of thiols with unsaturated hydrocarbons was first reported by Posner<sup>1</sup>, who treated thiophenol and benzylthiol with a variety of olefins at room temperature in the presence of acetic and sulfuric acids. With simple olefins, conjugated and nonconjugated, addition of fragments of the thiol produced by scission of the S-H link proceeded readily and, at asymmetrically substituted double bonds, in opposition to Markovnikov's rule:  $\text{CR}'\text{R}''\text{:CHR}''' + \text{SPh} \rightarrow \text{CHR}'\text{R}''\text{-CH(SPh)R}'''$ . More complex nonconjugated olefins (terpinolene and sylvestrene) showed depressed reactivity in that addition occurred at only one double bond, and the highly conjugated systems, stilbene and diphenylbutadiene, failed to react at all. Ashworth and Burkhardt<sup>2</sup> confirmed Posner's formulation of the styrene-thiophenol reaction, and pointed out the catalytic activity of sunlight and the inhibition induced by small amounts of piperidine<sup>3</sup>. Ipatieff and others<sup>4</sup> investigated the reaction of thiophenol and ethanethiol and propylene, isobutylene, trimethylethylene, and isopropylethylene at 100–150°, and found that, although addition products abnormal with respect to Markovnikov's rule were formed in the absence of catalysts, yet the presence of sulfuric acid, contrary to Posner's findings<sup>1</sup>, reversed the orientation of the addition and led to normal products. Contemporaneously, Jones and Reid<sup>5</sup> and Kharasch, Reid, and Mayo<sup>6</sup> showed that traces of peroxides, either as present normally in unsaturated hydrocarbons or as added ascaridole, strongly catalyze the abnormal addition, and that quinol effectively impedes the reaction. Mayo and Walling<sup>7</sup> have proposed a free-radical chain-reaction mechanism, but kinetic evidence on which to found a detailed reaction scheme is so far lacking.

The object of the present work was the preparation of commercially useful rubber derivatives, since this method, with its apparent specificity of double-bond attack and mild reaction conditions, offers a means of introducing various groups along the chain with a high probability of preserving the molecular character of the original polymer. The only other work along these lines is due to Holmberg<sup>8</sup>, whose observations of interaction between thioglycolic acid and rubber, balata, and gutta-percha are, however, of dubious significance (see below). This paper records the reactions of thioglycolic, thiophenol, and isopentanethiol with dihydromyrcene (diisoprene), squalene (a hexaisoprene), and rubber, and with the simple olefins, cyclohexene and 1-methylcyclohexene. Experiments with the latter not only permit unequivocal identification of the reaction products by chemical methods, but serve to emphasize an interesting and surprising variation in reactivity among this series of olefins.

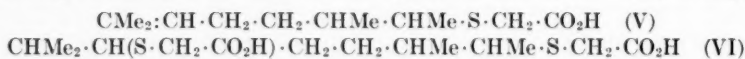
\* Reprinted from the *Journal of the Chemical Society*, 1947, pages 36–40.

*Reactions of thioglycolic acid.*—Although cyclohexene, 1-methylcyclohexene, and dihydromyrcene are immiscible with the thiol, on shaking equivalent amounts of ordinary laboratory specimens at room temperature a vigorous and highly exothermic reaction occurs immediately. When the olefins were freshly distilled in an atmosphere of nitrogen, the reaction was inappreciable, but proceeded almost explosively when a little ascaridole was added. On the other hand, no reaction occurred on mixing squalene with thioglycolic acid containing peroxide, and rubber (which is physically unaffected by the acid) failed to react even under highly favorable peroxidic conditions or irradiation with ultraviolet light.

The first three olefins gave liquid addition products in almost the theoretical yields. From cyclohexene was obtained *cyclohexylthioglycolic acid*,  $C_6H_{11} \cdot S \cdot CH_2 \cdot CO_2H$ , characterized by oxidation to the crystalline *sulfone*,  $C_6H_{11} \cdot SO_2 \cdot CH_2 \cdot CO_2H$ .

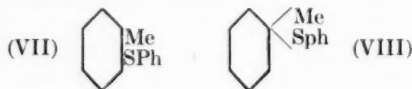


1-Methylcyclohexene gave a corresponding *methyl homolog*, b. p.  $135^\circ/0.1$  mm., which can either be the normal product (I) or the abnormal isomer (III), and which yields a crystalline *sulfone*, m. p.  $96^\circ$ , on oxidation (*i.e.*, either II or IV). Reaction of 1-methylcyclohexanol with thioglycolic acid under acidic conditions produced a *sulfide*, which must be (I), oxidizable to the *sulfone* (II), m. p.  $85^\circ$ , which gave a considerable m. p. depression on admixture with its isomer<sup>9</sup>, m. p.  $96^\circ$ . The sulfone synthesized *via* the olefin must, therefore, be (IV), and its parent sulfide the abnormal addition product (II). The normal sulfide was also obtained by reaction of the olefin and thioglycolic acid in 75% sulfuric acid at  $0^\circ$ , thus supporting Ipatieff's conclusions already mentioned concerning the directive influence of an acidic environment. Dihydromyrcene



yielded two liquid *sulfides* corresponding to the mono- or di-addition compounds (V) and (VI)<sup>10</sup>. The *sulfone* derived from (VI) was analytically pure, but failed to crystallize.

*Reactions of thiophenol.*—Both cyclohexenes and dihydromyrcene, squalene and rubber dissolve in thiophenol, without noticeable evolution of heat. Irradiation of the solution at room temperature with a quartz mercury-vapor lamp for a few hours initiated reactions with the first four olefins and produced high yields of sulfides, but again rubber was almost completely resistant. Cyclohexene gave the liquid *sulfide*,  $C_6H_{11} \cdot SPh$ , characterized by the crystal-



line *sulfone*,  $C_6H_{11} \cdot SO_2Ph$ . 1-Methylcyclohexene gave the *sulfide* (VII) whose constitution was established by the non-identity of its derived *sulfone* with that synthesized from the authentically normal *sulfide* (VIII). Ultraviolet absorption also served as a specific criterion for distinguishing the sulfides. The spectrum of (VII), resembling that of cyclohexylphenyl sulfide has an

intense band with a maximum at 2585 Å. ( $\epsilon = 7000$ ) arising from conjugation of the sulfur atom with the adjacent phenyl group. Models show that in (VIII) steric hindrance by the methyl group interferes with the coplanarity of the sulfur valencies and the benzene ring which is essential to full development of such conjugation and, in agreement with this, the associated band is practically absent from the spectrum of (VIII). Analogously to its reaction with the thioglycolic acid, dihydromyrcene yielded a mixture of *mono*- and *di*-adducts. The pale yellow viscous reaction product from squalene was freed from excess of thiol by heating to 100° on a high-vacuum line, and analysis then showed moderate incorporation of thiophenol, but no attempt was made to separate and purify the mixture of phenyl squalene sulfides<sup>11</sup>.

**Reactions of isopentaneithiol.**—Irradiation with ultraviolet light of a mixture of cyclohexene and the thiol yields the *sulfide*  $C_6H_{11} \cdot SC_5H_{11}$ , which can be oxidized to the *sulfone*  $C_6H_{11} \cdot SO_2 \cdot C_5H_{11}$ . The corresponding *sulfide* from 1-methylcyclohexene was obtained by heating a mixture of the reagents to 100° for 12 hours, but since the derived sulfone failed to crystallize, it is not possible to prove whether normal or abnormal addition occurs. A mixture of dihydromyrcene and the thiol, left in daylight at room temperature for a year, gave a mixture of *mono*- and *di*-adducts. Squalene behaved as described for cyclohexene, but again rubber remained inert.

**Discussion.**—The general characteristics of the reactions described above are typical of the peroxide-catalyzed additions so extensively explored by Kharasch and his school<sup>12</sup>. The most notable feature is the inexplicable reluctance of rubber to react with either of the thiols—the case of thiophenol, an excellent solvent for rubber, effectively disproving any suggestion that insufficient contact of the reactants is responsible, as indeed might be argued with thioglycolic acid. Holmberg's claim<sup>8</sup> to have obtained reaction with the latter compound by immersing rubber strips for up to two years at room temperature is open to question. According to him, the rubber, completely insoluble at the start, gradually swells and eventually dissolves, forming a homogeneous solution. The author's experience is that small pieces of rubber in excess of the thiol, with or without ascaridole, sealed up in a vacuum and left for two years, are inappreciably swollen, much less dissolved. Holmberg's mixtures presumably had access to air, however, and catalytic activity by oxygen may have promoted the reported addition. On the other hand, thioglycolic acid itself is readily oxidized on atmospheric exposure<sup>13</sup>, so reactions secondary to this may have initiated the observed changes. The inertness of rubber seems to represent the extreme of a reactivity trend, cyclohexene > dihydromyrcene > squalene > rubber, of as yet unknown origin.

As regards the activity of the addenda, the order appears qualitatively as, thioglycolic acid > thiophenol ~ isopentaneithiol, which parallels the strength of the related carboxylic acids, malonic, benzoic, and isovaleric. This suggests that the ease of active hydrogen atom and proton removal is similarly conditioned, and that the rupture of the S-H link provides the main contribution to the activation energy and heat of reaction of the addition process.

### SUMMARY

Under peroxidic conditions, cyclohexene and 1-methylcyclohexene add very readily the fragments formed by scission of the S-H bonds in the thiols named in the title. At the asymmetrically substituted double bond, the orientation of addition is shown to proceed contrary to Markovnikov's rule.



Dihydromyrcene and squalene undergo similar but less vigorous reactions, and rubber does not react.

#### EXPERIMENTAL

*Reactions with thioglycolic acid.*—(A) Cyclohexene (8.2 g.) was shaken with thioglycolic acid (9.2 g.) for 15 minutes; a homogeneous solution resulted. After removal of traces of unchanged reactants at 100° in a vacuum, distillation yielded *cyclohexylthioglycolic acid* (14.5 g.), b. p. 122°/0.1 mm. (Found: C, 55.3; H, 8.1; S, 18.1; equiv., 176.  $C_8H_{14}O_2S$  requires C, 55.2; H, 8.05; S, 18.4%; equiv., 174).

To the above acid (5 g.) in chloroform (60 cc.) were added ice, 3 *N* sulfuric acid (170 cc.), and then powdered potassium permanganate (8 g.) in small portions with constant shaking. The mixture was then allowed to attain room temperature, decolorized with aqueous sodium bisulfite, the chloroform layer separated, and the aqueous layer extracted with more chloroform. The combined extracts were dried ( $Na_2SO_4$ ) and concentrated to give the crude solid *sulfone*, which crystallized from benzene in glistening needles, m. p. 82° (Found: C, 46.4; H, 6.8; S, 15.25; equiv., 200.  $C_8H_{14}O_4S$  requires C, 46.6; H, 6.8; S, 15.5%; equiv., 206).

(B) 1-Methylcyclohexene.—The olefin (9.6 g.) reacted vigorously with the thio acid (9.2 g.), the product, isolated by distillation, being 2-methylcyclohexylthioglycolic acid (III), b. p. 135°/0.1 mm. (Found: C, 56.9; H, 8.6; S, 16.6; equiv., 191.  $C_9H_{16}O_2S$  requires C, 57.4; H, 8.4; S, 17.0%; equiv., 188).

Oxidation of this sulfide (5 g.) exactly as described for the cyclohexyl homolog gave 4.5 g. of the crude *sulfone* (IV), which separated from benzene-light petroleum (b. p. 100–120°) as colorless plates, m. p. 96° (Found: C, 48.7; H 7.3; S, 14.15; equiv., 216.  $C_9H_{16}O_4S$  requires C, 49.1; H, 7.3; S, 14.55%; equiv., 220).

*Preparation of 1-methylcyclohexylthioglycolic acid (I).*—(1) 1-Methylcyclohexanol (21 g.) was heated with thioglycolic acid (24 g.) and 2 *N* hydrochloric acid (220 cc.) for 4 hours at 110°. The cooled mixture was extracted three times with chloroform, the extracts dried ( $Na_2SO_4$ ), then concentrated to yield a yellow oil (15 g.), which was dissolved in 2 *N* potassium hydroxide, and any unchanged methylcyclohexanol removed by ether extraction. Distillation of the purified oil, regenerated from the alkaline solution by acidification, gave 1-methylcyclohexylthioglycolic acid, b. p. 147°/0.1 mm. (Found: C, 57.5; H, 8.4; S, 16.5%; equiv., 189). (2) Thioglycolic acid (4.6 g.) was slowly added to a rapidly stirred solution of 1-methylcyclohexene (9.6 g.) in 75% aqueous sulfuric acid (50 g.) cooled to 0°. When addition was complete, the mixture was allowed to warm to room temperature, and stirring continued for a further 15 minutes. The product isolated by ether extraction was purified *via* an aqueous alkaline solution as under (1) and then distilled; b. p. 142°/0.1 mm. (Found: C, 57.3; H, 8.6; S, 16.7%; equiv., 193).

The *sulfone* (II) of the acid (I), prepared in the usual manner and recrystallized from benzene-light petroleum (b. p. 60–80°), had m. p. 85° (Found: C, 49.9; H, 7.4; S, 14.2%; equiv., 218). A mixed m. p. with the 2-methyl isomer (IV) showed a depression of 20–25°.

(C) *Dihydromyrcene*.—(1) The olefin (10 g.) (Found: C, 87.05; H, 13.0%; I.V., 364. Calc. for  $C_{10}H_{18}$ : C, 86.9; H, 13.1%; I.V., 368) was shaken for 30 minutes with the quantity (6.5 g.) of thio acid required to saturate one double bond; the resulting homogeneous solution was diluted with benzene (200 cc.), and unchanged thioglycolic acid removed by several washings with water.



Fractionation of the oil obtained from the benzene solution gave dihydromyrcene, b. p.  $<140^{\circ}/14$  mm. (1.2 g.), and (2) *dihydromyrcene monothioglycolic acid* (V), b. p.  $170^{\circ}/0.1$  mm. (7.9 g.) (Found: C, 62.55; H, 9.6; S, 13.8; equiv., 234.  $C_{12}H_{22}O_2S$  requires C, 62.6; H, 9.6; S, 13.9%; equiv., 230); (3) high-boiling residue of uncertain composition (5.4 g.). The reaction was repeated but with excess of thioglycolic acid, the product being taken up in benzene and freed from unchanged acid as before. Concentration of the benzene solution gave a viscous oil which, after being kept at  $100^{\circ}$  in a high vacuum to remove any hydrocarbon, analyzed correctly for *dihydromyrcene bis(thioglycolic acid)* (VI) (Found: C, 52.15; H, 8.0; S, 19.65.  $C_{14}H_{26}O_4S_2$  requires C, 52.25; H, 8.1; S, 19.8%).

Oxidation of the latter acid (VI), carried out in the usual way, yielded a viscous gum which failed to crystallize, although analysis showed it to be the desired *sulfone* (Found: C, 43.2; H, 6.8; S, 16.0.  $C_{14}H_{26}O_6S_2$  requires C, 43.5; H, 6.7; S, 16.6%).

(D) *Squalene*.—The hydrocarbon (1 g.) was shaken with the acid (3 g.) and a little ascaridole (0.05 g.) for several weeks at room temperature. The mixture, which remained heterogeneous, was worked up as described for the dihydromyrcene products, but gave only unchanged squalene.

(E) *Rubber*.—(1) Sol rubber (1 g.) was dissolved in benzene (20 cc.) containing thioglycolic acid (2 g.) and ascaridole (0.05 g.), and the solution sealed under a vacuum in a pyrex tube 1.5 cm. in diameter. The tube was irradiated for 20 hrs. by a Hanovia S. 500 mercury-vapor lamp placed 6 inches distant. The product, obtained by precipitation with ethyl alcohol followed by extraction (Soxhlet) with alcohol in an atmosphere of nitrogen for 24 hrs., was a white rubber superficially indistinguishable from the starting material (Found: S, 1.7%, which corresponds to 3.8% addition). (2) A similar reaction mixture to that in (1) was sealed in a vacuum and kept in the laboratory for 2 years; a virtually unchanged rubber resulted (Found: S, 1.1%, i.e., 2.4% addition). (3) The rubber (1 g.), cut into small pieces, was suspended in thioglycolic acid (10 g.) containing ascaridole (0.05 g.), and the mixture sealed off under a vacuum, and left for 2 years. At the end of this time, the rubber nodules, which showed no sign of change, were removed and well washed with alcohol (Found: S, 0.75%).

*Reactions with thiophenol*.—(A) *Cyclohexene*.—The olefin (8.2 g.) was dissolved in thiophenol (11 g.), and the solution irradiated with the mercury lamp for 8 hours. The product, freed from unchanged reactants, was a yellow oil (16 g.) which consisted almost entirely of *cyclohexylphenyl sulfide*, b. p.  $108^{\circ}/0.1$  mm. (Found: C, 74.95; H, 8.35; S, 16.6.  $C_{12}H_{16}S$  requires C, 75.0; H, 8.3; S, 16.65%). Light absorption in cyclohexane showed  $\lambda_{max}$ , 2575 Å. ( $\epsilon = 5800$ ). Oxidation of the sulfide in the usual way gave the *sulfone*, which crystallized from methyl alcohol in colorless cubes, m. p.  $74^{\circ}$  (Found: C, 64.1; H, 7.2; S, 14.1.  $C_{12}H_{16}O_2S$  requires C, 64.25; H, 7.1; S, 14.3%).

(B) *1-Methylcyclohexene*.—Prepared from the hydrocarbon (9.6 g.) and the thiol (11 g.) just as was the cyclohexene derivative, *2-methylcyclohexylphenyl sulfide* (VII) had b. p.  $120^{\circ}/0.1$  mm. (Found: C, 75.6; H, 8.75; S, 15.35.  $C_{13}H_{18}S$  requires C, 75.6; H, 8.75; S, 15.55%);  $\lambda_{max}$ , 2585 Å. ( $\epsilon = 7000$ ) in cyclohexane.

The *sulfone*, crystallized from methyl alcohol in needles, m. p.  $108^{\circ}$  (Found: C, 65.5; H, 7.6; S, 13.25.  $C_{13}H_{18}O_2S$  requires C, 65.5; H, 7.6; S, 13.45%).

*Preparation of 1-methylcyclohexylphenyl sulfide* (VIII).—1-Methylcyclohexene (9.6 g.) was treated with thiophenol (5.5 g.) in the presence of 75%

aqueous sulfuric acid (50 g.), as described for the preparation of 1-methylcyclohexylthioglycolic acid, method (2). The required *sulfide* was obtained as an oil, b. p. 123°/0.1 mm. (Found: C, 75.6; H, 8.8; S, 15.25%), with  $\lambda_{\text{max}}$ . 2680 Å. ( $\epsilon = 1500$ ) in cyclohexane. The corresponding *sulfone* crystallized from light petroleum (b. p. 80–100°) in needles, m. p. 76° (Found: C, 65.5; H, 7.6; S, 13.3%). A mixed m. p. with the 2-methyl isomer showed a depression of 20–30°.

(C) *Dihydromyrcene*.—Irradiation of a solution of the hydrocarbon (7 g.) in the thiol (10 g.) with the mercury lamp for 8 hrs. yielded an oil (12.2 g.) separable by fractional distillation into *phenyldihydromyrcene sulfide* (8 g.), b. p. 135°/0.05 mm. (Found: C, 77.2; H, 9.65; S, 13.1.  $\text{C}_{16}\text{H}_{24}\text{S}$  requires C, 77.4; H, 9.7; S, 12.9%), and *dihydromyrcene-bis(phenyl sulfide)* (3.4 g.), a viscous syrup, b. p. 185°/0.05 mm. (Found: C, 73.5; H, 8.25; S, 17.85.  $\text{C}_{22}\text{H}_{30}\text{S}_2$  requires C, 73.8; H, 8.4; S, 17.85%).

(D) *Squalene*.—The hydrocarbon (1 g.), thiophenol (2 g.), and ascaridole (0.05 g.) were sealed in a vacuum and irradiated with ultraviolet light for 8 hrs. Removal of unchanged reactants by heating at 100° at  $10^{-5}$  mm. left a mixture evidently consisting of phenylsqualene sulfides (Found: C, 76.6; H, 8.95; S, 13.8. Calc. for 56% addition: C, 77.4; H, 9.0; S, 13.8%).

(E) *Rubber*.—(1) A solution of sol rubber (1 g.), the thiol (2 g.), benzene (20 cc.), and ascaridole (0.05 g.) was sealed under vacuum in a Pyrex tube and irradiated as before for 16 hours. The product, practically unchanged rubber, had S, 1.45% (i.e., corresponding to 3.25% addition). (2) A solution of rubber in the thiol (10 g.) without benzene was now employed, and the reaction conditions of (1) repeated. The product had S, 1.8%. (3) A similar solution to that used in (2) was sealed in a vacuum and left at room temperature for 2 years. Again, the rubber had undergone little change (Found: S, 1.15%).

*Reactions with isopentanthiol*.—(A) *Cyclohexene*.—A solution of the olefin (8 g.) in the thio (8 g.) was irradiated for 8 hours, the product freed from the starting materials by heating to 100° at 25 mm. pressure, and the residual oil (12 g.) distilled. The exclusive product was *cyclohexylisoamyl sulfide*, b. p. 120°/12 mm. (Found: C, 70.9; H, 11.85; S, 17.5.  $\text{C}_{11}\text{H}_{22}\text{S}$  requires C, 71.0; H, 11.8; S, 17.2%). The usual oxidation procedure gave the *sulfone* as an oil which crystallized with some difficulty from ice-cold light petroleum (b. p. 40–60°) as flat leaflets, m. p. 54–56° (Found: C, 59.5; H, 10.0; S, 14.7.  $\text{C}_{11}\text{H}_{22}\text{O}_2\text{S}$  requires C, 60.5; H, 10.1; S, 14.6%).

(B) *1-Methylcyclohexene*.—The olefin (10 g.) and thiol (10 g.) were refluxed together for 12 hours. When freed from excess of reactants, the sole product was a *methylcyclohexylisoamyl sulfide*, b. p. 124°/10 mm., which is probably the 2-methyl isomer, although this was not formally proved (Found: S, 16.1.  $\text{C}_{12}\text{H}_{24}\text{S}$  requires S, 16.0%). By the normal procedure, the *sulfone* was obtained as an oil, b. p. 149°/0.1 mm. (Found: C, 61.6; H, 10.3; S, 13.5.  $\text{C}_{12}\text{H}_{24}\text{O}_2\text{S}$  requires C, 62.1; H, 10.35; S, 13.8%).

(C) *Dihydromyrcene*.—The hydrocarbon (10 g.) was dissolved in the thiol (16 g.), and the solution sealed in a vacuum, and left in the laboratory for a year. Fractionation of the product gave: (1) unchanged reactants contaminated with a little sulfide, b. p. <148°/10 mm. (6.2 g.); (2) *Isoamyldihydromyrcene sulfide* (Found: C, 73.7; H, 12.3; S, 13.8.  $\text{C}_{15}\text{H}_{30}\text{S}$  requires C, 74.4; H, 12.4; S, 13.2%), b. p. 158°/10 mm. (6.3 g.); (3) material of b. p. <170°/0.05 mm. consisting of a mixture of (2) and (4); and (4) *dihydromyrcene-bis(isoamyl sulfide)* (Found: C, 69.35; H, 12.05; S, 17.9.  $\text{C}_{20}\text{H}_{42}\text{S}_2$  requires C, 69.4; H, 12.8; S, 18.5%), b. p. 171–174°/0.05 mm. (12.0 g.).

(D) *Squalene*.—Squalene (1 g.), the thiol (2 g.), and ascaridole (0.05 g.) were sealed together in a vacuum and irradiated for 16 hours with the mercury-vapor lamp. The product, freed from unchanged reactants, was a viscous oil (1.8 g.) (Found: S, 16.5. Calc. for 76% addition: S, 16.5%).

(E) *Rubber*.—(1) Sol rubber (1 g.), dissolved in benzene (20 cc.) containing the thiol (2 g.) and ascaridole (0.1 g.), was sealed in a Pyrex tube under a vacuum and irradiated as before for 16 hours. The solution had then set to a stiff gel, but on trituration with alcohol and drying in a vacuum an insignificantly changed rubber of low sulfur content was obtained (0.9 g.) (Found: S, 0.95%). (2) A similar solution to that used in (1) was sealed in a vacuum and kept at room temperature for 2 years. Isolated by alcohol precipitation, the rubber was practically unchanged (Found: S, 0.7%).

#### ACKNOWLEDGMENT

I thank W. T. Chambers and (Miss) H. Rhodes for carrying out the microanalyses, and H. P. Koch for the spectrographic measurements in this work, which forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

#### REFERENCES

- <sup>1</sup> Posner, *Ber.* **38**, 646 (1905).
- <sup>2</sup> Ashworth and Burkhardt, *J. Chem. Soc.* **1928**, p. 1791.
- <sup>3</sup> Carothers, *J. Am. Chem. Soc.* **55**, 2008 (1933).
- <sup>4</sup> Ipatieff and others, *J. Am. Chem. Soc.* **60**, 2731 (1938); **61**, 71 (1939).
- <sup>5</sup> Jones and Reid, *J. Am. Chem. Soc.* **60**, 2452 (1938).
- <sup>6</sup> Kharasch, Reid and Mayo, *Chemistry and Industry* **57**, 752 (1938).
- <sup>7</sup> Mayo and Walling, *Chem. Reviews* **27**, 387 (1940).
- <sup>8</sup> Holmberg, *Ber.* **65**, 1349 (1932).
- <sup>9</sup> Since this work was completed, Hellström and Sandström have published a paper (*Svensk. Kem. Tids.* **54**, 149 (1942)) describing work on a series of reactions which led to the formation of the sulfones (II) and (IV); however, whereas (II), for which the m.p. 84–85° is given, is correctly designated, a compound, undoubtedly (IV), having m.p. 92–93°, is described as a sulfonic acid.
- <sup>10</sup> No attempt is made to distinguish between the two different isomers which result from additions at either of the double bonds, and in this and the following paper, the formulas for the mono-adducts are arbitrary in this respect.
- <sup>11</sup> To avoid other ambiguity and for general simplicity, the polyisoprene adducts are designated throughout this and the following paper as, *e.g.*, phenylsqualene sulfide, it being understood that a hydrogen atom is added, together with the thio radical, to give the respective sulfur derivative of a saturated hydrocarbon as shown in the various formulas.
- <sup>12</sup> For a complete list of references, see Mayo and Walling, *Chem. Reviews* **27**, 387 (1940).
- <sup>13</sup> Klason, *Ber.* **14**, 410 (1881).

## STRUCTURAL CHANGES IN RUBBERS BROUGHT ABOUT BY MOLECULAR OXYGEN \*

B. DOGADKIN

LOMONOSOV INSTITUTE OF FINE CHEMICAL TECHNOLOGY, MOSCOW, U. S. S. R.

The interaction of rubber with oxygen has great significance in the chemistry and technology of rubbers. It is enough to point out that this action appears as a fundamental process in the aging of rubber wares. Further, as shown by Busse<sup>1</sup>, Cotton<sup>2</sup> and others, the normal process of mastication of natural rubber takes place only in the presence of atmospheric oxygen. In vulcanization, as well as the interaction of rubber with the vulcanizing agent, there is also interaction with molecular oxygen contained in the rubber mixture, which, as we were the first to show<sup>3</sup>, may be one of the reasons for the appearance of the vulcanization optimum. Finally, the reclaiming of rubber by thermal treatment is also obviously to a greater or less extent connected with the action of oxygen.

All the above mentioned processes are accompanied by changes in the properties of rubber and, consequently, by changes in its structure. These changes may be not only different in character in individual cases, but sometimes directly contradictory. Thus the mastication of natural rubber results in an increase of solubility, a decrease of strength and in other phenomena characteristic of the degradation of macromolecular compounds. The mastication of sodium-butadiene rubber is accompanied by a lowering of the content of soluble phase.

The object of this work is to explain the nature of the structural changes caused by the interaction of different types of rubber with oxygen and to connect these changes with the conditions of the process and with the initial structure of the polymer. This aspect of the question has been little studied in the literature on the oxidation of rubber, attention having been concentrated up to the present on the investigation of the kinetics of the process.

The nature of the changes of physical properties on oxidation of rubbers is determined on the one hand by thermodynamic conditions (temperature, concentration of reacting components); on the other hand it depends on the type of polymer. Essential factors, also, are the extent of interaction of the polymer with oxygen and the directing action of other substances present, which may contain, *e.g.*, carbonyl or amino groups. The intrusion of oxygen into the molecular chains of the polymer results, in the last resort, in the formation of polar groups, which necessarily influences the intensity of intermolecular forces and consequently, produces changes of such properties as solubility, strength, density, etc. On the other hand, the simple addition of oxygen and the creation of oxygen-containing polar groups, unaccompanied by changes in the sizes and structures of the molecules, can influence the physical properties only when the process has gone a long way. In particular, the energy of the

\* Reprinted from the *Transactions of the Faraday Society*, Vol. 32, No. 12, pages 709-19, December 1946, as a translation by Gwyn Williams from the *Zhurnal Obshchei Khimii* (*Journal of General Chemistry* (U. S. S. R.)), Vol. 15, No. 3, pages 177-186, 1945. The paper was presented at the Conference on Macromolecular Compounds at the Academy of Sciences of the U. S. S. R., February 8, 1943.

intramolecular forces of attraction in natural rubber increases by approximately 30 per cent when all the double bonds are replaced by epoxide oxygen. And for this it is necessary that the weight of added oxygen should amount to approximately 24 per cent of the weight of the rubber. In all the above technical processes, the change of physical properties of rubbers sets in much earlier, when the amount of absorbed oxygen is only a few per cent (up to 3 per cent).

To explain this fact it is evidently necessary to assume that the action of oxygen causes structural changes in the rubber; and that these changes become appreciable at quite small oxygen content of the reaction products, because the proportion between the average molecular weight of the rubber and the oxygen weight is of the order of magnitude of tens of thousands.

As the action of molecular oxygen is directed to the double bonds or to carbon atoms standing in the  $\alpha$ -position to the carbon of a double bond, the nature of the structural changes on oxidation of rubber depends above all on the disposition of the double bonds in the molecular chains of the polymer. From this point of view, rubber polymers may be divided into three types.

*Type A.*—Linear polymers containing double bonds in the main chains. Examples of such polymers are natural rubber,  $\alpha$ -polychloroprene, the thermal polymer of butadiene, etc.

*Type B.*—Spatial polymers whose chains are united by cross-links. The ethylene bonds in polymers of this type are distributed throughout its whole volume. Examples of such polymers are the insoluble fraction of the butadiene emulsion polymer, and the products of copolymerization of butadiene and styrene, and also, obviously,  $\mu$ -polychloroprene.

*Type C.*—Linear polymers containing double bonds in side chains, e.g., sodium-butadiene rubber.

Naturally there exist intermediate cases between these types.

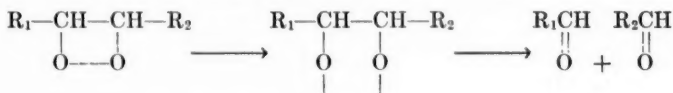
It is possible that, in general, completely regular polymers do not exist. We assign a given type of rubber to a polymer type according to which of the above structures predominates in it.

The results of interaction of molecular oxygen with a rubber of a given type are quite characteristic.

It should be remarked, however, that in the following discussion we neglect special features in the structure of the monomeric groups. These may have a marked influence on the interaction of the polymer with oxygen, especially if these monomeric groups contain halogen atoms, the CN group, etc. We neglect also the possibility of resonance between the double bonds in the polymer chains, which, however, has mainly kinetic significance.

#### INTERACTION OF OXYGEN WITH LINEAR POLYMERS CONTAINING DOUBLE BONDS IN THE MAIN CHAINS (TYPE A)

Characteristic changes in the initial stage of oxidation of linear polymers, containing double bonds in the main chains, are decrease in strength, increase in plasticity, the growth of viscosity, increase of solubility and fall in the viscosity of solutions. All these phenomena point to disintegration of the molecular chains, which may be interpreted<sup>4</sup> as a result of the breakdown of peroxide compounds according to the following scheme:





This reaction represents only one side of the oxidation process, but it appears to be the most important because with it is connected the structural alteration of the rubber which shortens the molecular chains. Actually the process is far more complicated, for among the products of degradation of natural rubber, along with the aldehydes and ketones envisaged by this scheme, hydroxyl and carboxyl groups, ethers and epoxides are observed in significant quantities. The formation of polar degradation products is proved also by the sharp lowering of the interfacial tension between benzene solutions of rubber and a water boundary, after illumination with a quartz lamp in an atmosphere of oxygen<sup>5</sup> (Figure 1).

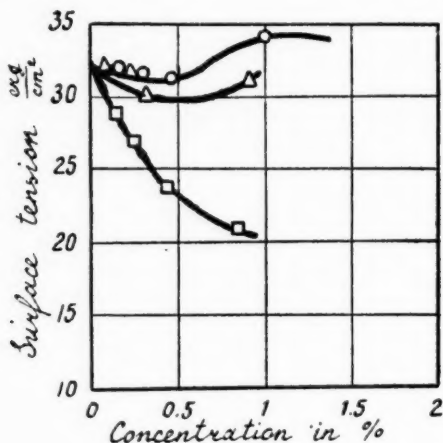


Fig. 1.—Isotherm of surface tension of rubber solution: ○—○ before irradiation by means of ultraviolet light; Δ—Δ after irradiation in nitrogen; □—□ after irradiation in air.

In this way the presence of double bonds in the main chains of the polymer is responsible for the relative ease with which these polymers undergo oxidative degradation. It also explains why rubbers of type A are easily masticated, soften on aging, display a tendency to fall in the viscosity of solutions, etc. With this property should also be connected the phenomenon of the vulcanization optimum, so characteristic of natural rubber. We have put forward the suggestion<sup>3</sup> that the presence of minima on the kinetic curves for vulcanization (for example, on the curve for the chloroform extract), or of maxima (*e.g.*, for the curve of breaking strain) is connected with the fact that, under vulcanization conditions, two or more oppositely directed processes take place—a building-up of structure, *i.e.*, union of the polymer chains under the influence of the vulcanizing agent—and a degradation, *i.e.*, disintegration of the chains under the action of oxygen. These processes have different kinetics and the total effect in different cases may express itself on the curve as a minimum or maximum in relation to the forms of the superimposed curves. Polymers of type C, incapable of oxidative degradation, do not display a vulcanization optimum for some properties.

This is seen in Figure 2, in which are presented the changes of relative and residual extension in mixtures of natural (type A) and sodium-butadiene (type C) rubbers after long vulcanization periods—up to 400 minutes.



The changes of physical properties described, connected with the degradation of rubber, are observed as already mentioned in the initial stages of oxidation, when the amount of absorbed oxygen does not exceed 2-5 per cent. Further oxidation is accompanied in certain cases by opposite changes: the softened, viscid rubber becomes hard; its solubility in nonassociated liquids decreases. These changes may be explained as an association of the chains owing to the presence of oxygen-containing polar groups; and, as it seems to us, by secondary reactions resulting in a recombination of the fragments of the molecular chains, with formation of longer chains, or even with the formation

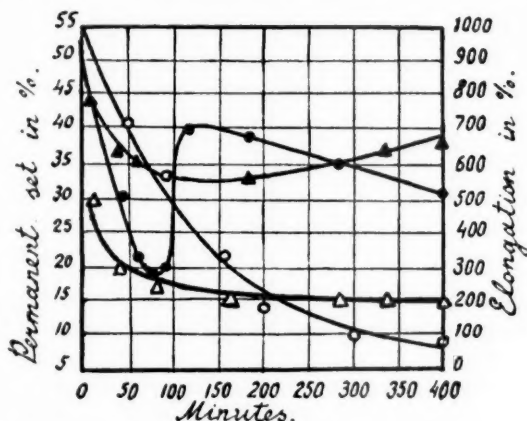


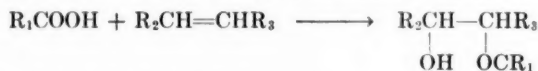
Fig. 2.—Change of elongation during vulcanization: ●—● natural rubber; ○—○ sodium-butadiene rubber. Change of permanent set: ▲—▲ natural rubber, Δ—Δ sodium-butadiene rubber.

of spatial netlike structures. Recombination of the chains is possible as a result of the following reactions:

- (1) Esterification, with combination of hydroxyl and carboxyl groups



- (2) Combination of carboxyl groups with double bonds



- (3) Combination of hydroxyl and epoxide groups



The carboxyl, hydroxyl and epoxide groups required for these reactions accumulate in the first stages of oxidation. The mechanism of their formation is discussed in the work of Farmer<sup>6</sup>, and their presence in the products of oxidation of rubber has been confirmed by us<sup>5</sup> and with special fullness and care in the work of Hilton<sup>7</sup>, who subjected the rubbone product, obtained through catalytic oxidation of rubber, to analytic study. One of the fundamental conditions for the occurrence of secondary recombination reactions of the chains appears to be the temperature of the process.

According to Kohman<sup>8</sup>, if the oxidation reaction proceeds at 80° C, then the formation of hard insoluble products begins when the rubber has absorbed from 22–24 per cent of oxygen. According to our experiments at 150° this occurs after absorption of 10–12 per cent, *i.e.*, 0.22–0.27 mole of oxygen per  $C_5H_8$  group. Since the milling of natural rubber and its normal aging take place at relatively low temperatures (not higher than 80°), practically only the first stage of the degradation of its molecular chains is observed in these cases.

#### INTERACTION OF OXYGEN WITH SPATIAL POLYMERS (TYPE B)

The fundamental characteristic of polymers with spatial structure is their insolubility in ordinary rubber solvents. The gel fractions of butadiene rubber and the copolymer of butadiene and styrene, investigated by us, did not dissolve, on careful exclusion of oxygen, either at high temperatures (up to 143°) or with prolonged action of the solvent—up to 3 years. As solvents we used benzene and its derivatives, decalin, cyclohexane, piperidine, alcohols, ethers, esters, etc. In all, twenty solvents were tried. Binary mixtures, containing polar solvents, in particular a mixture of toluene and ethyl alcohol, a mixture of benzene and butyl alcohol or pyridine in different proportions also brought about no dissolution. This fact is in clear contradiction to the statements of Pummerer<sup>9</sup> and of Meyer<sup>10</sup>, according to which the insoluble fraction of natural rubber forms as a result of the association of oxidized chains of the soluble fraction. Solution took place only when the solvent was saturated with molecular oxygen. This was brought about by heating 0.1 gram of rubber and 10 cc. of xylene in a sealed tube filled with oxygen. The amount of substance going into solution was determined as the dry residue in the liquid phase after centrifuging. The kinetics of dissolution and dispersion are presented in Figure 3: the greater part of the process is expressed by a straight line,

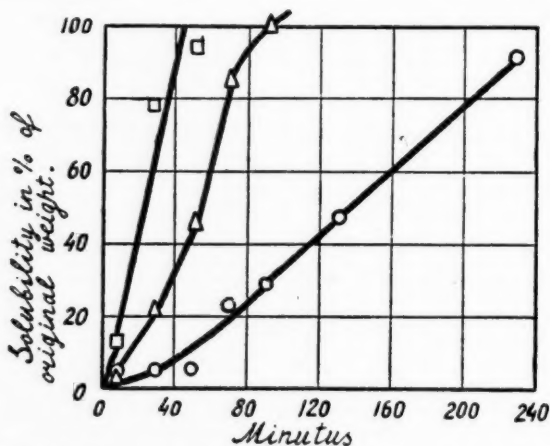


Fig. 3.—Kinetics of solution (dispersion) of the insoluble fraction of rubber during oxidation: □—□ at 135° C, Δ—Δ at 125° C, ○—○ at 115° C.

and may be interpreted as heterogeneous, taking place with maintenance of the extent of surface of the solid phase. The temperature dependence of the kinetic constants is represented in Figure 4. The apparent energy of activation

is calculated from the data of this curve to be 27,200 calories per mole, which serves as a direct indication that the degradation of the polymer is a chemical process and not a thermal disaggregation of its secondary colloid structure.

Thus, the interaction of oxygen with polymers of spatial structure to a certain stage is accompanied by their disintegration. The chemical side of the process is, in general, analogous to that described for the initial stage of oxidation of a polymer of type A. Oxygen attacks the double bonds, distributed throughout the volume of the polymer, and when such attacks attain a certain frequency, particles separate from the polymer mass and go into the solvent.

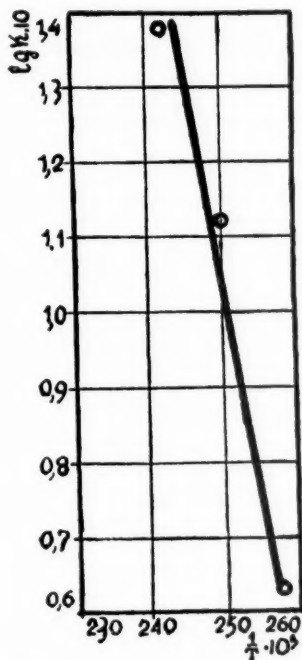


FIG. 4.—Relation between temperature and kinetic constant of solution of rubber.

In contrast to the degradation of type A polymers, in this case it is not individual molecular chains, but spatial structures of more or less nearly spherical form, which go into solution. For this reason, and also because of their tight structure, the particles are less solvated than the particles of linear polymers. The characteristics indicated reveal themselves in the fact that solutions of the products of oxidative degradation of spatial polymers show over a wide range of concentrations a Rayleigh type of light scattering and obedience to the Einstein-Poiseuille law. This is shown in Figure 5, in which the magnitude of the light scattering is expressed in units of absolute turbidity, measured with a Pulfrich photometer.

Analogous structural changes are observed when the action of oxygen on rubbers of spatial structure takes place during milling. In this case a remarkably characteristic phenomenon is observed, sharply distinguishing the behavior of these rubbers from that of natural rubber. When the latter is

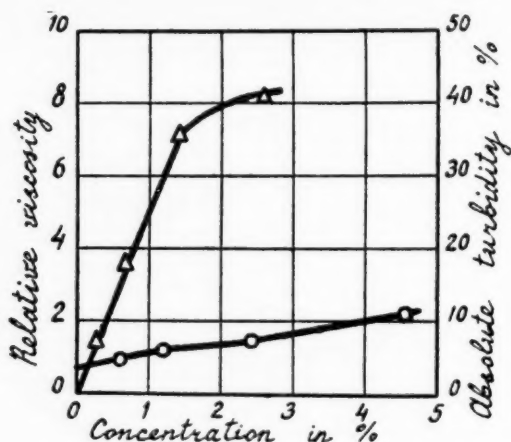


Fig. 5.—Viscosity and turbidity of solution of rubber:  
O—O viscosity, Δ—Δ absolute turbidity.

masticated there is a continuous and sharp fall in the viscosity of solutions as a result of progressive degradation of its molecular chains. In the mastication of spatial polymers the viscosity of that part of the rubber which goes into solution practically does not change during the whole period of mastication (Table I).

TABLE I  
CHANGES OF VISCOSITY OF BENZENE SOLUTIONS OF BUTADIENE EMULSION  
POLYMER AND OF ITS INSOLUBLE FRACTION DURING MILLING

Substance	Time of milling (min.)	Concentration (percentage)	Relative viscosity
Rubber	0	1.01	3.28
	5	1.01	3.35
	30	1.05	3.50
	60	0.98	3.45
Insoluble fraction	5	1.02	2.88
	40	0.98	2.60
	120	0.98	2.32

This peculiarity is understandable if it is recalled that, under the conditions of mastication, the destruction of the spatial structure proceeds under the simultaneous influence of oxygen and of purely mechanical agencies.

This effect which we have observed of the solution of polymers with spatial structure as a result of the action of molecular oxygen has, it seems to us, a direct relation to the processes of reclaiming rubber by the classical alkali method and, even more so, by the oil reclaim method. The spatial structure characteristic of the vulcanized product evidently disintegrates, as in the case which we have described, under the influence of molecular oxygen.

#### INTERACTION OF OXYGEN WITH LINEAR POLYMERS CONTAINING DOUBLE BONDS IN SIDE CHAINS (TYPE C)

The absence of double bonds in the main chains of polymers of this type excludes the possibility of their oxidative degradation. (We do not take into

account here the probability of disintegration of saturated paraffin chains for which other thermodynamic conditions are necessary.) Addition of oxygen takes place in the side chains. In particular, with sodium-butadiene rubber, this process takes place in the lateral vinyl groups and, when they disintegrate, formaldehyde, formic acid and carbon dioxide should separate at an early stage of oxidation. The main chain of the polymer preserves its dimensions and configuration. The average molecular weight of the rubber and the character of the distribution curve remain without change. Thus, changes of physical properties connected with diminution of molecular weight, increase of solubility, plasticity, etc., which are characteristic of the initial stages for polymers of types A and B, do not take place in this case. The formation in the side chains of carboxyl, hydroxyl and other oxygen-containing groups results in each molecule of the oxidized product becoming polyfunctional and capable of secondary esterification and other reactions of oxygen-containing groups discussed earlier. As a result of the polyfunctionality of the molecules, such reactions lead either to the formation of spatial structures or to the formation of branched molecules having higher average molecular weights. In this case, therefore, oxygen plays the part of a structure building factor. The change in structure is revealed by changes of the physical properties of the polymer; at an early stage of the process the product of oxidation of rubber of type C becomes insoluble, hard, and stronger than the initial polymer.

A similar kind of change in the properties of polymers with double bonds in side chains was investigated by us<sup>11</sup> and also by Zaionchkovski and Pisarenko<sup>12</sup> and others for sodium-butadiene rubber. After heating a mixture of this rubber with gas carbon (a hundred parts of rubber to sixty parts of carbon) at a temperature of 190° to 200°, the following changes took place: a sharp increase in strength, a fall of relative and residual extension, and a fall in solubility. Heating of a similar mixture containing natural rubber (type A polymer) does not cause such changes; this brings out sharply the difference in the behavior of a polymer with double bonds in the main chains (type A) from that of a polymer with double bonds in side chains (type C).

To separate purely thermal effects on the structure of rubber from the structural effects caused by oxidative processes, we made experiments by heating pure sodium-butadiene rubber in oxygen and in nitrogen at 145–150°. Three different procedures were used with the aim of excluding as sharply as possible the action of oxygen in the nitrogen experiments. With only one of these were the essential conditions achieved, allowing heating without access of oxygen. In this case the properties of the rubber suffered no noticeable changes whatever.

In Figure 6 is represented the change of swelling and solubility of sodium-butadiene rubber after heating in air at 145–150°. The resulting changes are characteristic of the formation of spatial structures. Figure 7 gives comparative data for the changes of mechanical properties on heating the rubber in air and in an atmosphere of nitrogen. Since in the last case no changes of solubility and mechanical properties were observed (data in Table II), the part played by oxidative processes in the building of structure admits of no doubt. This appears with special clarity from an examination of Figure 8, in which is represented the functional relation between the increase of breaking strain and the fall of solubility of the specimen on the one hand and the amount of oxygen absorbed by the rubber on the other hand. The amount of absorbed oxygen was determined as the increase in weight of the films and should be corrected to take account of volatile products of oxidation.

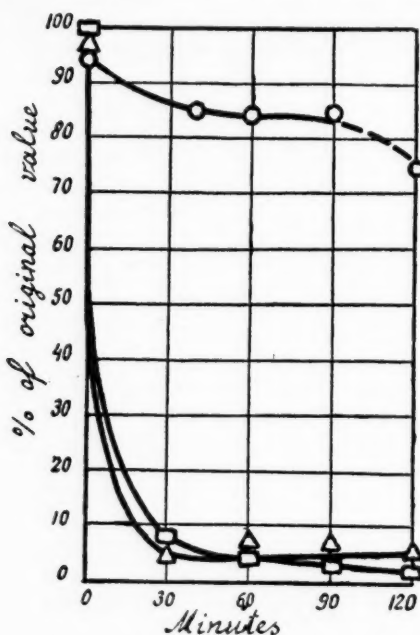


FIG. 6.—Change of properties of sodium-butadiene rubber during heating in air:  $\circ$ — $\circ$  unsaturation;  $\square$ — $\square$  solubility in benzene;  $\Delta$ — $\Delta$  chloroform extract.

The heating of sodium-butadiene rubber in an atmosphere of oxygen at the temperatures indicated is always accompanied by the separation of water. This may be regarded as an indirect indication of the occurrence of esterification processes underlying the formation of spatial structures. However, it is essential to bear in mind that other steps in the oxidative process, in particular the decomposition of hydroperoxides, may lead to the same result. In any case, the elimination of water as a result of the combination of two polymer

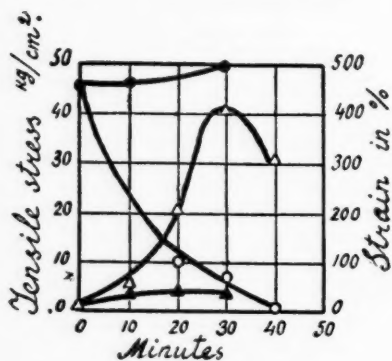


FIG. 7.—Change in tensile properties of sodium-butadiene rubber during heating: tensile strength  $\Delta$ — $\Delta$  in air,  $\blacktriangle$ — $\blacktriangle$  in nitrogen, elongation  $\circ$ — $\circ$  in air,  $\bullet$ — $\bullet$  in nitrogen.

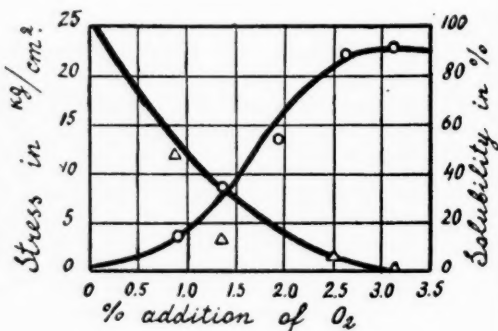


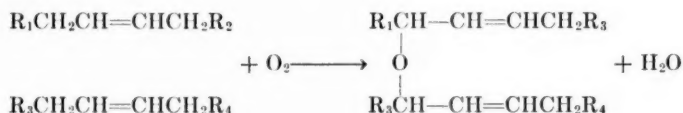
FIG. 8.—Change of stress and solubility of sodium-butadiene rubber during oxidation:  $\circ$ — $\circ$  stress;  $\Delta$ — $\Delta$  solubility.



TABLE II  
CHANGES OF PROPERTIES OF SODIUM-BUTADIENE RUBBER ON HEATING  
AT 142°–148° C IN NITROGEN AND IN AIR

Medium	Time of heating (min.)	Breaking strain (kg. per sq. cm.)	Relative extension (percentage)	Residual extension (percentage)	Solubility in benzene (percentage)
Air	0	1.93	440	10	100
	10	4.75	690	10	47.9
	20	20.3	120	0	16.63
	30	41.0	50	0	4.68
	40	31.0	—	—	—
Nitrogen	0	1.93	440	10	100
	10	2.40	450	10	100
	20	2.37	350	10	99.5
	30	2.18	500	10	99.2

chains, with oxygen playing the part of a hydrogen acceptor according to the following scheme:



appears to us at present less probable, with each reaction proceeding as though trimolecular.

Of the accessory phenomena accompanying the interaction of oxygen with sodium-butadiene rubber, it is essential to single out the change in character of luminescence. The lilac color of unworked rubber changes to light green. A similar type of change of luminescence is observed in the normal vulcanization of the rubber by sulfur.

As already remarked, regular polymers, *i.e.*, polymers whose chains are constructed strictly according to one plan, are encountered extremely rarely. Most frequently a given type of rubber contains chains of different types. Sodium-butadiene rubber, as well as the predominating content of type C, also contain structures with double bonds in the main chains (type A). The behavior of such rubbers may naturally depart to a known extent from the above schemes. Thus in the oxidation of hard specimens of sodium-butadiene rubber a weakly expressed softening stage of the rubber is observed, appearing in our experiments as a flow of the product on the walls of the bulbs. At an earlier stage the normal change for a polymer of type C into elastic and then solid product occurs. This softening stage is evidently connected with the presence in the polymer of a structure with double bonds in the main chains (type A), which, on the basis of ozonization data, amounts to 20 per cent of the carbon skeleton. So far as the structure with double bonds in side chains predominates (from ozonization data up to 80 per cent of the carbon skeleton), the further development of the process follows the characteristics described for a polymer of type C.

#### EXPERIMENTAL

*Determination of the interfacial tension at the boundary of a benzene solution of rubber against water.*—For these experiments we used a rubber specially purified by the method described previously<sup>7</sup>. A benzene solution of this rubber was exposed to illumination by a quartz lamp for forty minutes in a specially constructed apparatus, allowing the experiment to be carried out in

an atmosphere of nitrogen or of oxygen. The interfacial tension was determined by the method of maximum pressure in a bubble, in the apparatus described by Reh binder. The isotherm of interfacial tension at the boundary benzene solution—water for an unilluminated preparation shows a minimum, which we explained earlier<sup>3</sup>. Illumination in an atmosphere of nitrogen does not change the character of the isotherm (compare Figure 1). Illumination in an atmosphere of oxygen results in a sharp decrease of the interfacial tension.

*Determination of solubility and investigation of the kinetics of dispersion (dissolution) of spatial polymers.*—As an example of a spatial polymer, whose individual chains are joined by cross-links, we investigated the benzene-insoluble fraction of the product of the emulsion polymerization of butadiene. The separation of this fraction took place under conditions designed to exclude, as far as possible, the action of atmospheric oxygen. The action of the solvent was studied in the following way. About 0.1 gram of the rubber was placed in a glass bulb, after which the bulb was repeatedly evacuated with an oil pump and filled with pure nitrogen. Then 10 cc. of the solvent, dried in nitrogen, was introduced, and the system again pumped out and filled with nitrogen. The sealing of the bulb took place in a continuous supply of nitrogen. The bulbs were heated in a glycerine bath for 72 hours at 100–145° C. Some of the bulbs were then kept at room temperature for three years. In these no visible changes of the swollen gel were observed. Determination of the dry residue showed no transfer of substance into the solvent. In the observation of the kinetics of dispersion of the spatial polymer under the action of oxygen, the bulbs with rubber and solvent (xylene) were filled with dry oxygen before sealing. Individual bulbs were heated for different times, and the amount of rubber which went into solution was determined as the dry residue in the solution, separated from the weighed insoluble portion by centrifugation or filtration through silk.

*Heating of sodium-butadiene rubber in an atmosphere of nitrogen and of oxygen.*—In one of the variants of procedure the experiments were carried out as follows. The sodium-butadiene polymer was prepared from pure butadiene, obtained by the decomposition of recrystallized tetrabromide and condensed in bulbs filled with nitrogen. The opening of the bulbs after polymerization, the alcohol washing of the polymer from sodium, and its solution, were carried out in a nitrogen cupboard in a continuous current of pure nitrogen. There the polymer solutions were poured on to glass plates smeared with glycerine. The plates were previously boiled in ethyl alcohol in a stream of nitrogen and preserved under alcohol dried in nitrogen. On drying, the films of polymer were removed from the glass and charged into cylindrical vessels closed by cleaned lids with a three-way tap. These vessels, before being placed in the nitrogen cupboard, were heated to 150–200°, with alternate pumping out of gas and admission of nitrogen to remove oxygen adsorbed on the walls. After charging with the films of polymer, the cylinders were taken from the nitrogen cupboard, again evacuated, and filled with pure nitrogen. The latter was purified by passage through columns of oxygen absorbers (quinol or sodium hydrosulfite solution) and over copper gauze at 600°. All liquids used in the operations were dried in nitrogen. The films were heated by placing the cylinders in a thermostat at 143°. After different periods of time the strength of the film on a Smirnov dynamometer, its solubility and its iodine number were determined. Films for heating in oxygen were prepared in a similar way. In the latter case the amount of oxygen combined was determined by the weight increment of the film.

## SUMMARY

The nature of the changes of physical properties of rubber resulting from oxidation processes is determined by its initial structure and also by the conditions of the process (temperature, concentration of reagents, extent of their interaction, type of reaction, etc.).

In the interaction of molecular oxygen with linear polymers containing double bonds in the main chains, *e.g.*, with natural rubber, a disintegration of the chains takes place in the initial stages, as a result of which an increase of solubility, a decrease of strength, an increase of plasticity and a decrease in the viscosity of solutions of the rubber are observed.

The decrease in solubility and the increase of strength and elasticity set in at that stage of oxidation at which local links of ether type are formed between individual chains, or at which the accumulation of polar groups containing oxygen increases to a noticeable extent the intensity of intermolecular attractive forces.

In the interaction of molecular oxygen with spatial (network) polymers, *e.g.*, with the insoluble fraction of butadiene and butadiene-styrene polymers, with a solvent medium, there occurs a disintegration of structure and passage (dispersion) into the solvent medium. The solutions obtained contain massive particles of spherical form and display over a wide range of concentrations a Rayleigh type of light scattering and obedience to the law of Einstein and Poiseuille.

The chemical nature of the dissolution of spatial polymers is confirmed by the magnitude of the activation energy of the process (27,000 calories per mole).

A similar breakdown of spatial structures occurs in the milling of rubbers of this type, in which, in contrast to cases of mastication of linear polymers, the viscosity of solutions of spatial polymers does not change during the time of mastication.

In the interaction of molecular oxygen with linear polymers containing double bonds in side chains, *e.g.*, with sodium-butadiene rubber, the principal effect which takes place is the secondary process of combination of chains to spatial structures, resulting in the observation of a decrease of solubility, and an increase of strength and elastic properties of the polymer. This formation of spatial structures in the second stage of oxidation is facilitated by the poly-functionality of the products of the initial stage of oxidation of the original polymer.

The structural changes described, proceeding under the action of oxygen, constitute one of the causes of the appearance of the vulcanization optimum.

## REFERENCES

- <sup>1</sup> Busse, *Ind. Eng. Chem.* **24**, 140 (1932).
- <sup>2</sup> Cotton, *Trans. Inst. Rubber Ind.* **6**, 487 (1931).
- <sup>3</sup> Dogadkin, "Studies on Rubber", Vol. 1, p. 295.
- <sup>4</sup> Dogadkin, *Uspekhi Khimii*, **1936**, No. 5, p. 499.
- <sup>5</sup> Dogadkin and Panchenkov, *Kolloid-Z.* **65**, 350 (1933).
- <sup>6</sup> Farmer, Bloomfield, Sundralingam and Sutton, *RUBBER CHEM. TECH.* **15**, 756 (1942).
- <sup>7</sup> Hilton, *Trans. Inst. Rubber Ind.* **17**, 319 (1942); *RUBBER CHEM. TECH.* **15**, 965 (1942).
- <sup>8</sup> Kohlman, *J. Phys. Chem.* **33**, 26 (1929).
- <sup>9</sup> Pummerer, in Memmler "Handbuch der Kautschukwissenschaft", p. 184.
- <sup>10</sup> Meyer and Wertheim, *Helv. Chem. Acta* **24**, 217 (1941).
- <sup>11</sup> Dogadkin and Feldstein, *Kauchuk i Rezina*, **1939**, No. 12, p. 12.
- <sup>12</sup> Zaionchkovski and Pisarenko, *Kozhevenno-Obuvnaya Prom. U.S.S.R.* **1940**, No. 7.

## THE ACTION OF BENZOYL PEROXIDE ON NATURAL RUBBER IN SOLUTION \*

PATRICE COMPAGNON AND ANDRÉ DELALANDE

INSTITUT FRANÇAIS DU CAOUTCHOUC, 42 RUE SCHEFFER, PARIS, FRANCE

An earlier publication<sup>1</sup> described experiments on the combination of active ethylene compounds, such as maleic anhydride and acrylonitrile, with rubber in solution under the influence of benzoyl peroxide. Control experiments on the action of benzoyl peroxide alone under the same conditions were carried out also, and from the results it was possible to come to certain conclusions. Since then, the reactions of unsaturated compounds with rubber have been investigated more extensively, and further experiments have been carried out on the action of benzoyl peroxide alone. The authors believe that it is of interest to discuss these observations at the present time, for it is not intended to continue with any systematic study of this problem, which actually is only of secondary importance as far as the main purpose of the investigation under way is concerned.

Furthermore, it is felt that some of the experimental results may be of importance to other investigators who have studied, in the past few years, the photogelation and oxidation of rubber from the theoretical viewpoint. Finally, in the work already cited<sup>1</sup>, no mention was made of the important part played by oxygen, even when in very low percentages, and this led to an incorrect interpretation of the phenomena, for which it is well to make amends at this time.

The vulcanizing action of benzoyl peroxide on rubber is well known. It was first reported by Ostromislensky<sup>2</sup> as far back as 1915 when he described the vulcanizing action of organic peroxides in general and particularly the action of nitro compounds. Since that time, various investigators<sup>3</sup> have interested themselves in this reaction, but no practical applications seem ever to have been made of it. Recently Farmer and his collaborators<sup>4</sup>, basing their work on the properties of benzoyl peroxide and on the lability of the  $\alpha$ -methylenic hydrogen atoms of rubber hydrocarbon, have shown that the phenyl and benzoyl radicals which are formed by the thermal decomposition of benzoyl peroxide are capable of attaching themselves to rubber at the same time that chemical bonds are formed between the chains of the higher polymer, with or without an accompanying decrease in unsaturation. The vulcanizing action of benzoyl peroxide is explained in this way, for all investigators are in accord in believing that vulcanization is a result of the formation of bridges between molecules of rubber hydrocarbon.

It is known, likewise, that, under certain conditions, benzoyl peroxide promotes the degradation of rubber, a phenomenon which is the reverse of vulcanization. This phenomenon is specifically mentioned in several patents, notably in one of the Hollandsche Draad en Kabel Fabriek<sup>5</sup>, which states that raw rubber is plasticized by the addition of a small proportion of benzoyl

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 24, No. 1, pages 4-7, January 1947.

peroxide, *e.g.*, 1 per cent, during milling. The temperature is maintained at 80–100° C. The batch of rubber is plasticized until a product of the desired molecular weight is obtained, which may be liquid at elevated temperatures and semiliquid at ordinary temperatures.

When benzoyl peroxide acts on rubber in solution, it is observed that, depending on the conditions, there is either a vulcanizing effect, which is manifest by gelation of the solution, or a degradation effect. In the latter case, the rubber which is precipitated from the solution by the addition of alcohol is recovered in the form of a viscous liquid somewhat like Rubbone<sup>6</sup>, but without the drying tendency of the latter. However, under conditions which will be pointed out later, a third type of reaction of benzoyl peroxide also takes place, which is not vulcanization, for the solution remains fluid; nor is it degradation, at least in any evident way, although no molecular-weight measurements were made. Here the rubber when precipitated from the solution has the same general appearance that it had before being dissolved. An explanation of this phenomenon will be offered later.

The phenomenon of gelation has already been described, particularly by Bock<sup>7</sup>, and the phenomenon of degradation in solution has been described by Shimada<sup>8</sup>. The latter showed that both accelerators of vulcanization and the vulcanizing agents of Ostromislensky lower the viscosity of rubber solutions.

It should be pointed out that the possibility of the same reagent acting on rubber in two opposite ways, *i.e.*, bringing about either an increase or a decrease in molecular weight, has been suggested by Spence and Ferry<sup>9</sup>. The experiments described by these investigators were concerned with the effects of small proportions of benzoquinone and of other quinones in latex. In a later publication<sup>10</sup>, they point out also that benzoyl peroxide has the same action. Nevertheless the effects obtained in solutions by the present authors were much more pronounced. The present authors have not studied the effects of quinones in general, and therefore it is still not possible to say whether the results obtained with benzoyl peroxide would be obtained with solutions of these reagents.

The three modes of action of benzoyl peroxide indicated above depend, for a given concentration of rubber and of benzoyl peroxide, on the effects of light, temperature, and the presence or total absence of oxygen. First of all it is well to review the phenomena which are observed as they are influenced by these three factors. Except when pointed out as otherwise, the reactions were carried out in 3 per cent solutions of rubber (*i.e.*, 3 grams of rubber in 100 cc. of solution).

#### ACTION OF BENZOYL PEROXIDE IN THE ABSENCE OF BOTH OXYGEN AND LIGHT

As a general rule, the degradation brought about by the action of benzoyl peroxide is evident only when oxygen is present at the same time. In the experiments to be described, the results were obtained in the laboratory under conditions whereby atmospheric oxygen was excluded as rigorously as was possible.

The samples of rubber and benzoyl peroxide were put in crystal glass tubes, which were evacuated to 0.001 mm. The solvent, from a vessel from which air had likewise been expelled, was distilled into the tubes, and the latter were then sealed<sup>11</sup>. The tubes were shaken until their contents were homogeneous; they were then heated in an oven, with exclusion of light. The first rubber tested



was first latex crepe which had been masticated for 10 minutes at room temperature. Some of the experiments, repeated with purified rubber (by acetone extraction, followed by two successive solutions and precipitations), led to the same results.

*Action of heat and of solvent.*—When a solution of rubber in toluene (in 3 per cent concentration as already mentioned) was treated with 1 per cent of benzoyl peroxide (by weight of the rubber) for 24 hours, the phenomenon of gelation, corresponding to the effect of vulcanization, becomes manifest between 70° and 110° C. Above this temperature range, the solution remains fluid, and the rubber recovered by precipitation with alcohol has the same appearance that it had originally.

It was observed also that the time necessary for gelation to become appreciable decreased progressively with increase in temperature. For example, with 8 per cent of benzoyl peroxide, the time of gelation at room temperature was several weeks, whereas at 110° C it was only a few minutes. However, as with 1 per cent of benzoyl peroxide, the more concentrated solution remained fluid at higher temperatures, *e.g.*, at 130° C, but at this concentration the phenomenon was not so general, for it depended likewise on the mastication of rubber before solution, as will be shown later.

Finally the solvent plays an active part in the phenomena, for with small proportions of benzoyl peroxide, gelation continued up to higher temperatures in benzene than in toluene or with 8 per cent of benzoyl peroxide. Actually only in toluene did gelation no longer take place at elevated temperatures.

It might be asked whether this failure to gel is not attributable to the possibility that benzoyl peroxide decomposes so rapidly that it cannot react. Experiments now in progress with *p*-bromobenzoyl peroxide lead one to reject this hypothesis, and it seems that there is, under the conditions, a fixation on the rubber of free radicals formed by dissociation of benzoyl peroxide<sup>12</sup> in preference to the formation of bridges between hydrocarbon molecules. It is not surprising that the nature of the solvent has an influence on the phenomenon, since, as is well known, solvents have a specific effect on the dissociation constants of compounds which are donors of free radicals<sup>13</sup>.

*Influence of the benzoyl peroxide content.*—As might be expected, the tendency to gel is a function of the benzoyl peroxide content. For example, it was observed that, at 85° C, the threshold of gelation of a 3 per cent solution of rubber in benzene was with 1 per cent of benzoyl peroxide. Furthermore the data in Table 1 show that, at this temperature, the rate of formation of a gel varies with the percentage of benzoyl peroxide (based on the rubber). The right-hand column, which gives the swelling in benzene of the dried products (obtained by drying the gels in a vacuum at room temperature) of the gels formed by heating for the same length of time, *viz.*, 20 hours, will give an idea of the state of vulcanization.

TABLE 1

Benzoyl peroxide (percentage)	Time of gelation	Limit of swelling in benzene (percentage by volume)
0.4	5 hrs.	indeterminable
1	1 hr.	4.0
5	30 min.	2.3
10	15 min.	2.7

*Influence of the concentration of rubber and of the time of mastication of the rubber.*—Experiments carried out close to the limiting temperature at which



gelation no longer takes place showed that an increase in concentration of the rubber promotes the phenomenon of gelation. On the contrary, an increase in the time of mastication to which the rubber is subjected before solution retards gelation, as may be seen from Table 2, the data of which represent toluene solutions of rubber, containing 8 per cent of benzoyl peroxide, and heated 20 hours at 130° C.

TABLE 2

Time of mastication of the rubber (min.)	Concentration of rubber (g. per 100 cc. of solution)	Appearance
5	3	gel
10	3	partial gel
30	3	solution
30	3	gel
75	3	solution
75	5	solution
75	10	gel

It should be added that, at 80/90° C, definite gelation took place in all the solutions. It would be interesting to know whether the gels which were formed at 130° C would no longer be formed if the temperature were raised to a still higher point. However, no experiments were carried out under these conditions.

*Influence of light.*—No experiments on the simultaneous action of light and of benzoyl peroxide in sealed tubes from which air was excluded have been carried out by the present authors. However, it should be mentioned that Stevens<sup>14</sup> has shown that light activates the vulcanizing effect of benzoyl peroxide on rubber in solution. According to observations by the present authors, which are to be described later, it would seem that this can be so only under such conditions that oxygen takes no part in the reaction.

#### ACTION OF BENZOYL PEROXIDE IN THE PRESENCE OF OXYGEN

The experiments described in the previous work<sup>1</sup> are of importance in connection with the results to be described. In these earlier experiments, flasks surmounted by reflux condensers were used, and under such conditions contact with air was sufficient to make its effect evident, as was subsequently proved. It was found in the earlier experiments that, in the presence of light, benzoyl peroxide caused degradation of the rubber, whereas in reality light only intensified the combined action of benzoyl peroxide and of air, which is observable even in darkness. The few experiments described below make this fact evident.

*Influence of atmospheric oxygen in the absence of light.*—It has already been shown that a 3 per cent solution of rubber in benzene containing 8 per cent of benzoyl peroxide (by weight of the rubber) gels rapidly around 100° C in the absence of air. Operating with a reflux condenser for the benzene or toluene, and simultaneously passing a current of air (at the rate of about two bubbles per second), there was no gelation, and the rubber underwent very marked degradation. When no air was bubbled through the solution and at the same time refluxing was sufficiently effective, gelation occurred in most cases; but when the refluxing was too slow, and especially when the temperature was lower than the boiling point of the solvent, diffusion of air into the receptacle was sufficient to bring about degradation of the rubber. Under such conditions gelation may actually take place in the bottom of the receptacle while the solution at the surface contains degraded rubber. When the receptacle was

washed out thoroughly with nitrogen previously bubbled through an alkaline solution of pyrogallol, gelation was in all cases complete. When the reaction mixture contained less benzoyl peroxide, *e.g.*, 1 per cent instead of 8 per cent (based on the rubber), there was always sufficient oxygen present to prevent gelation, even when the apparatus had been washed free of nitrogen. However, as might be expected, degradation of the rubber was less pronounced; instead of becoming semiliquid as it did with 8 per cent of benzoyl peroxide, the rubber remained solid after being dried, although very sticky.

In brief, then, it would appear that the smaller the proportion of benzoyl peroxide taking part in the reaction, the smaller is the percentage of oxygen necessary to prevent gelation.

*Influence of atmospheric oxygen in the presence of light.*—This problem is concerned only with the effect of diffused sunlight on solutions contained in glass vessels.

Under the particular experimental conditions, gelation took place in darkness, but no gelation in diffused light. The qualitative observations summarized below, which are based on experiments carried out at room temperature, show clearly the part played by light in the presence of benzoyl peroxide and air. In these experiments the solutions were kept in tubes open to the air.

(1) Light and benzoyl peroxide bring about, in solutions of rubber exposed to air, a very marked degradation of the rubber.

(2) Light alone, in the absence of air, likewise brings about degradation of rubber, as already described by Naunton<sup>15</sup>, but, other conditions being the same, to a less marked degree than in the preceding case.

(3) In darkness, benzoyl peroxide in the presence of air renders rubber slightly sticky at the end of several days.

(4) In the absence of benzoyl peroxide and of light, contact with air alone does not change the rubber appreciably in the same length of time.

These experiments are evidence that the profound degradation of rubber by oxygen in the presence of benzoyl peroxide is closely related to certain phenomena which, as recently shown in numerous publications by Farmer and his collaborators, directly involve the  $\alpha$ -methylenic hydrogen of the rubber hydrocarbon, *i.e.*, on the one hand, the action of benzoyl peroxide itself, and, on the other hand, the direct action of oxygen in light, with formation of a hydroperoxide. It is evident that when these two factors act simultaneously under normal conditions, degradation of the rubber hydrocarbon by oxygen is much more severe.

Finally it is now clear why rubber is degraded by hot mastication with benzoyl peroxide present. Under these conditions, there is intimate contact with air and, in addition, light has an opportunity to play its part. The question might also be asked if there is not a certain analogy between this phenomenon and the action of certain agents known as peptizing agents.

#### REFERENCES

- <sup>1</sup> Compagnon and Delalande, *Rev. gén. caoutchouc* **20**, 133 (1943).
- <sup>2</sup> Ostromislensky, *J. Russ. Phys.-Chem. Soc.* **47**, 1374, 1401, 1441, 1453, 1462, 1467, 1885, 1892, 1898, 1904, 1993, 1995 (1915).
- <sup>3</sup> King, *Met. Chem. Eng.* **15**, 231 (1916); Twiss, *J. Soc. Chem. Ind.* **36**, 782 (1917); **44**, 106T (1925); *Trans. Inst. Rubber Ind.* **3**, 398 (1928); Fisher and Gray, *Ind. Eng. Chem.* **20**, 294 (1928); Whitby, *Trans. Inst. Rubber Ind.* **5**, 184 (1929); **6**, 40 (1930); Bock, *Kautschuk* **7**, 224 (1931); Van Rossem, Dekker and Prawirodipoero, *Kautschuk* **7**, 202, 219 (1931); *RUBBER CHEM. TECH.* **5**, 97 (1932); Pummerer, *Kautschuk* **7**, 223 (1931).
- <sup>4</sup> Farmer, *Trans. Faraday Soc.* **38**, 342 (1942); Farmer and Michael, *J. Chem. Soc.* **1942**, p. 513.

- <sup>5</sup> N. V. Hollandsche Draad en Kabel Fabriek, French patent 860,640 (1941).  
<sup>6</sup> Popham, *Rev. gén. caoutchouc* **21**, 255 (1944).  
<sup>7</sup> Bock, *Kautschuk* **7**, 224 (1931).  
<sup>8</sup> Shimada, *J. Soc. Chem. Ind. Japan* **36**, 52B (1933).  
<sup>9</sup> Spence and Ferry, *J. Am. Chem. Soc.* **59**, 1648 (1937).  
<sup>10</sup> Spence and Ferry, *J. Soc. Chem. Ind.* **58**, 345T (1939).  
<sup>11</sup> Moureu and Dufraisse, *Inst. int. chim. Solvay*, 2<sup>o</sup> Cons. de Chimie, 1925, Gauthier-Villars, Paris, 1926, p. 578.  
<sup>12</sup> Farmer and Michael, *J. Chem. Soc.* **1942**, p. 513.  
<sup>13</sup> Gomberg and Sullivan, *J. Am. Chem. Soc.* **44**, 1822 (1922).  
<sup>14</sup> Stevens, in "Advances in Colloid Science", New York, 1946, Vol. 2, p. 367.  
<sup>15</sup> Naunton, *Trans. Faraday Soc.* **38**, 332 (1942).

# INFLUENCE OF STRUCTURE ON POLYMER LIQUID INTERACTION. I. RELATIVE AND ABSOLUTE VALUES OF SWELLING EQUILIBRIA \*

G. SALOMON AND G. J. VAN AMERONGEN

## INTRODUCTION

To reach a better understanding of the correlation between molecular structure and intermolecular attraction, a comparison was made of swelling equilibria. With this aim we studied the absolute value of the swelling equilibrium under the influence of polar and polarizable groups, which were introduced in solvents and polymers with different molecular structures. The influence of temperature, cross-linking, external pressure, and mechanical strain on the position of the equilibrium was also studied. Any general treatment of swelling is obviously limited by our present knowledge of the properties of liquid mixtures<sup>1</sup>. Experimentally, however, the study of high polymeric solutions and gels offers several advantages over that of ordinary liquids. Our experiments, designed to elucidate the structure of polymers, also reveal properties of some organic liquids which could not be observed easily by other means.

Results obtained with commercial rubbers will be given in this paper, while analogous measurements on a series of copolymers with increasing numbers of nitrile groups will be dealt with in a second paper.

## THEORETICAL

Since the theoretical and experimental evidence were compiled in an authoritative review by Gee<sup>2</sup>, only some special points essential for the understanding of our experiments will be presented. It is now generally recognized that the swelling of a polymer is caused primarily by a gain in entropy. This gain by far exceeds the entropy change occurring during the formation of regular and irregular solutions of low molecular compounds. As was first pointed out by Meyer<sup>3</sup>, this anomalous large change in entropy in high polymer solutions can be explained by assuming that only a small segment of the macromolecule acts as a kinetic unit. The elastomer-liquid system must, nevertheless, be considered as being typically irregular, since an abnormal entropy change, as well as heat effects, occur during formation. The apparently successful application of the theory<sup>4</sup>, developed by van Laar and Hildebrand<sup>5</sup> for regular solutions, to polymeric systems is in fact due to a rather rigid limitation of the type of gel under consideration.

If it is assumed that the entropy change involved in reaching a certain degree of swelling is the same for all systems, then the differences in swelling equilibria are due to differences in the heat terms. The magnitude of this heat term is strongly dependent on the presence and interaction of polarizable and polar groups. In most cases the liquid-polymer system absorbs heat during formation, as the result of which swelling is restricted. Gee assumes that the

\* Reprinted from the *Journal of Polymer Science*, Vol. 2, No. 4, pages 355-370, August 1947. This paper is Communication No. 62 of the Rubber-Stichting.

maximum degree of swelling in a three-dimensional network is reached in an athermic swollen system. Recent experimental evidence produced by Ferry, Gee, and Treloar<sup>6</sup>, however, makes it seem very probable that liquid-polymer interaction near the equilibrium in certain cases, *e.g.*, with chloroform, can also be accompanied by a release of heat.

The strength of intermolecular attraction depends, not only on the presence of polarizable and polar groups, but even more on the strength of London forces. Between hydrocarbons the latter depend on the availability of the molecular surface and decrease in the series  $\text{CH}_3 > \text{CH}_2 > \text{CH} > \text{C}$ , as is known from boiling point rules. Intermolecular attraction in molecules therefore increases with substitution of hydrogen by methyl groups, as can be seen from a comparison of the boiling points and heats of evaporation of, for example, pentane and 2-methylpentane. The great influence of these intermolecular attractions on the properties of polymer molecules is very clear in the case of gas diffusion through elastomers. The rate of diffusion of gases through an elastomer depends mainly on the interaction forces between the elastomer molecules and is, therefore, much lower in methylated elastomers<sup>7</sup> and in elastomers with polar groups.

Interaction of polar groups is a function of dipole strength, as well as of charge distribution on the molecular surface, which largely determines the properties of chloroform<sup>8</sup>. Association between like molecules in liquid chloroform is weak, since the charge is spread on the large surface of the chloroform, whereas the opposite charge is concentrated on the small C—H bond, the latter being difficultly accessible for the  $\text{CCl}_3$  group of other chloroform molecules. In all cases where such  $\text{CCl}_3$  groups can interact with an opposite charge of an unlike molecule, *e.g.*, nitrile, nitrate, or hydroxyl, strong dipole interaction occurs with release of heat<sup>9</sup>. It is for this reason that chloroform and similar molecules are very good solvents for polymers with polar or polarizable groups. The change in free energy of mixing cannot be correlated in such cases with the cohesive energy density of the components, since it depends on the strength of interaction between unlike molecules and is, therefore, an individual property of the system.

Stearic effects can assume extraordinary magnitudes in polymeric solutions. Toluene and benzene mix with the absorption of very small quantities of heat<sup>9</sup> whereas polystyrene dissolves in benzene with the release of 415 calories per gram of styrene, almost independent of the degree of polymerization<sup>10</sup>. This proves that the interaction between benzene and polystyrene is much stronger than between like or nearly like molecules. The maximum degree of swelling is influenced not only by liquid-polymer interaction, but also by the elastic counterpressure of the three-dimensional network<sup>11</sup>. It is essential, therefore, to compare gels with a similar three-dimensional structure. We have restricted our comparison to elastic materials. A strong indication that the gels have a similar degree of cross-linking may be derived from the fact that fully vulcanized elastomers show approximately equal maximum degrees of swelling in chloroform and other suitable solvents. Finally, the kinetic properties of the liquid phase must be taken into account. Swelling equilibria with liquified gases and high-boiling softeners (as the two extremes) may differ from those of the physically similar organic liquids discussed here.

In a qualitative comparison the scale used to express results is important; some authors compare weight or volume percentages. As soon as intermolecular attraction varies with the degree of swelling, however, a quantity converging toward unity for the limiting case of dissolution must be used; the volume frac-

tions are the quantities which represent the actual physical changes most adequately. Since the contraction of the swollen gels is not exactly known, such comparisons are somewhat less accurate than comparisons of weight fractions, which are used throughout this paper. Only in cases in which liquids of high specific gravity are compared will results be expressed in volume fractions.

### EXPERIMENTAL

The trade names and approximate chemical compositions of the polymers are summarized in Table I. Since Butyl rubber was not available, some experi-

TABLE I  
COMPOSITION OF ELASTOMERS

Name	Monomer	Approximate number of substituents on C <sub>4</sub> units
Natural rubber	Isoprene	1 CH <sub>3</sub>
Methyl rubber	2,3-Dimethylbutadiene	2 CH <sub>3</sub>
Oppanol B-200	Isobutene	4 CH <sub>3</sub>
Buna-S	Butadiene-styrene	0.3 C <sub>6</sub> H <sub>5</sub>
Neoprene-G	Chloroprene	1 Cl
Perbunan	Butadiene-acrylonitrile	0.3 CN
Perbunan-Extra	Butadiene-acrylonitrile	0.45 CN

ments with Oppanol (unvulcanized polyisobutylene) are included. The conditions of vulcanization are shown in Table II. The mechanical properties of

TABLE II  
CONDITIONS OF VULCANIZATION

	Natural rubber	Methyl rubber	Buna-S	Neoprene-G	Perbunan	Perbunan-Extra
Rubber	100	100	100	100	100	100
Sulfur	1.5	1.5	1.5		1.5	1.5
Zinc oxide	5	5	5	5	5	5
Vulkacit-AZ*	1.8		1.8		1.8	1.8
Vulkacit-P Extra N†		1.5				
Phenyl-β-naphthylamine	2	2	1		1	1
Stearic acid	1.5	1.5			2	2
Magnesium oxide				5		
Temperature of vulcanization (°C)	142	110	142	142	142	142
Time of vulcanization (minutes)	45	45	45	60	45	45

\* Probably diethylaminomercaptobenzothiazole.

† Probably zinc salt of ethylphenyldithiocarbamate.

the vulcanized samples and the swelling are independent of small variations in vulcanization time and temperature.

Except for Oppanol the polymers contain polarizable double bonds. Neoprene has a high concentration of a polar chloride group of moderate strength. Perbunan and Perbunan-Extra contain the strongly polar nitrile group in a relatively low and a somewhat higher concentration, respectively. In most cases we have omitted the swelling data for methyl rubber, since natural rubber and methyl rubber have very similar swelling properties. Since the swelling behavior of Neoprene is intermediate between that of natural rubber and of Perbunan, the measurements with Neoprene have been omitted in certain cases.



The purity of the liquids was controlled by measurements of the refractive index and boiling point. Special care was taken in the purification of aliphatic hydrocarbons because their impurities have considerably stronger solvent action. The method used for measuring the swelling was essentially the same as the one used by Whitby, Evans and Pasternack<sup>12</sup>.

Round plates of  $\pm 100$  mg. were cut from plates 1 mm. thick and placed in the liquid at 25° C. After a certain time the sample was removed from the liquid, adherent droplets were removed by drying with filter paper, and the sample was weighed in a stoppered flask. The increase in weight after one, three, and seven days was plotted against the time of swelling and the equilibrium calculated by extrapolation to zero time, after the method of Scott<sup>13</sup>. Equilibrium was reached after less than one day, and the increment observed was negligible in most cases. The absolute value of the equilibrium is influenced by the presence of 0-5 per cent of a soluble fraction, but all data are calculated on the weight of the original sample, since this uncertainty does not influence conclusions drawn from the comparisons.

#### INFLUENCE OF MOLECULAR STRUCTURE ON SWELLING EQUILIBRIUM

The well-known phenomenon of oil resistance caused by the association of polar groups in the polymers is illustrated in Figure 1, which shows that the

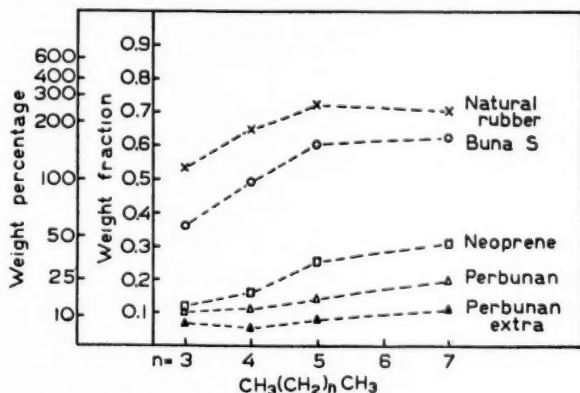


Fig. 1.—Swelling in aliphatic hydrocarbons.

swelling decreases in aliphatic hydrocarbons in proportion to the quantity and strength of the polarizable and polar groups in the elastomer. The interaction of natural rubber with the hydrocarbons decreases for the lower members of the series. It is interesting to note that, at ordinary pressure and 25° C, the solubility of methane in natural rubber, expressed as the weight fraction, is 0.0002. It may also be seen from Figure 1 that the swelling of natural rubber for the higher members of the series approaches a constant value, 0.7, which is considerably lower than the maximum degree of swelling in other solvents (see Figures 5, 9, and 10).

Figure 2 gives some information in the influence of the carbonyl group in the aliphatic chain of the solvent; the degree of association,  $\alpha$ , for the pure solvent<sup>14</sup> is also given. The shape of the curves clearly indicates the influence of the introduction of longer aliphatic chains, by which the polar carbonyl group is screened off. Although the lower ketones are only weak swelling agents

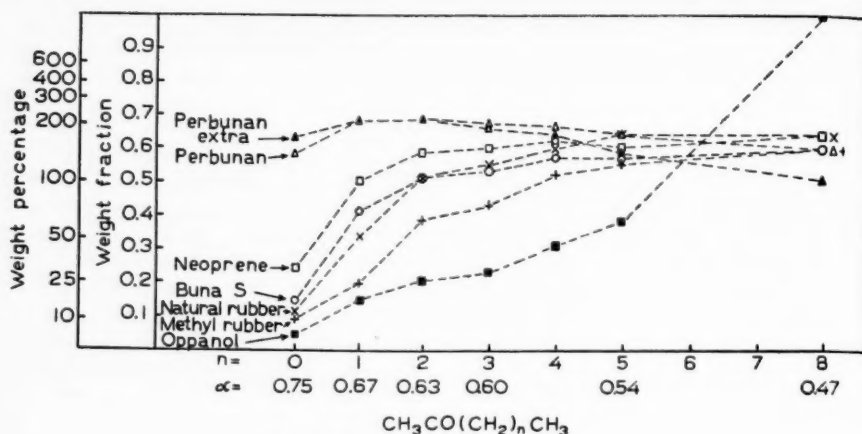


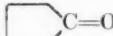


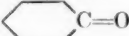

FIG. 2.—Swelling in methyl alkyl ketones.

for Oppanol, the action of methylnonyl ketone results in complete solvation. The same effect is apparent from the shape of the curves for the nonpolar rubbers. The maximum in the curve for Perbunan-Extra, giving the interaction with nitrile rubbers, illustrates the compensating influence of the three types of association:



More detailed conclusions on the influence of structure can be drawn from Table III. The position of the carbonyl group in the aliphatic chain is of minor importance, whereas cyclization produces a stronger solvent<sup>4</sup>.

TABLE III  
INFLUENCE OF MOLECULAR STRUCTURE ON SOLVENT POWER OF KETONES

Carbon atoms	Solvent	Swelling, weight fraction					
		Oppanol	Methyl rubber	Natural rubber	Buna-S	Perbunan	Perbunan-Extra
C <sub>4</sub>	C <sub>2</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub>	0.33	0.42	0.55	0.57	0.70	0.69
	CH <sub>3</sub> COC <sub>3</sub> H <sub>7</sub>	0.20	0.39	0.51	0.52	0.67	0.66
	 C=O	0.19	0.53	0.64	0.69	0.77	0.78
C <sub>5</sub>	CH <sub>3</sub> COC <sub>4</sub> H <sub>9</sub>	0.22	0.43	0.55	0.53	0.67	0.66
	CH <sub>3</sub> COC(CH <sub>3</sub> ) <sub>3</sub>	0.26	0.45	0.55	0.49	0.65	0.62
	CH <sub>3</sub> COCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	0.22	0.41	0.52	0.48	0.65	0.62
	 C=O	0.25	0.61	0.70	0.71	0.77	0.77
C <sub>6</sub>	CH <sub>3</sub> CO <sub>5</sub> H <sub>11</sub>	0.31	0.52	0.60	0.57	0.66	0.64
	CH <sub>3</sub> -  C=O	0.29	0.62	0.71	0.67	0.75	0.75
	 C=O	0.37	0.65	0.72	0.70	0.75	0.75
	 C=O	0.52	0.70	0.74	0.73	0.77	0.76

The close relationship between the polarity of groups and solvent power is illustrated by Figure 3. The introduction of polar groups in the liquid produces an increased swelling power for the polar elastomers and a reduced swelling power for the nonpolar elastomers, a situation quite different from the one encountered with the aliphatic hydrocarbons. We now encounter the case in which natural rubber has a swelling resistance contrary to that of Perbunan. The activity of nitrile and nitro groups in the solvent is the same. The difference between these strongly polar groups and the hydroxyl groups in alcohols is very striking, since the latter show little interaction, not only with the nonpolar rubbers, but also with the nitrile rubbers. Apparently, the hydrogen bond overshadows any nitrile-hydroxyl interaction. A comparison of a number of oxygen-containing liquids is given in Figure 4, which confirms conclusions drawn from Figure 3.

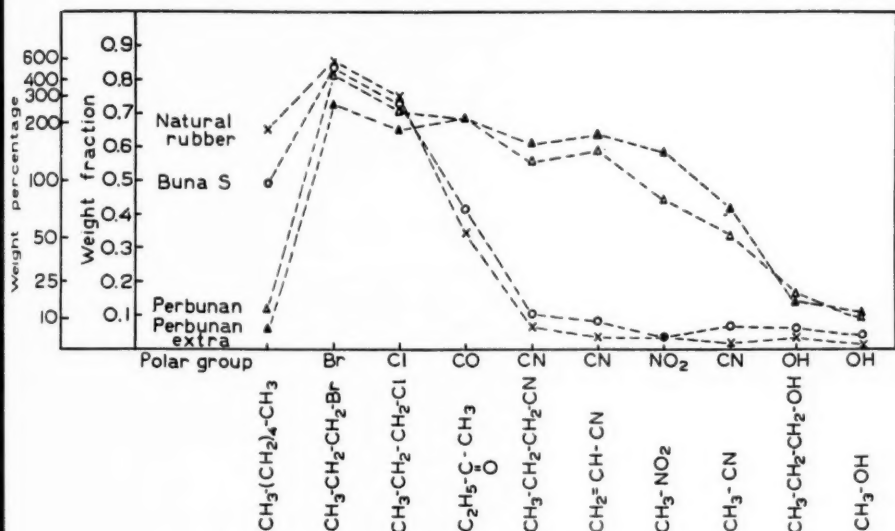


FIG. 3.—Influence of polar groups in the liquid on the swelling equilibrium.

Figure 5 illustrates the very pronounced influence of double bonds. The introduction of double bonds makes the molecules polarizable, which leads to a stronger interaction with the polar or polarizable elastomers. The swelling power of cyclohexane is unexpectedly high. Apparently, cyclization in the molecule favors its solvent action, which may be related to the diminished mobility of the methylene groups. The introduction of a double bond in cyclohexane produces a further increase in swelling power.

Table IV offers a comparison of some C<sub>10</sub> ring compounds; decalin takes an intermediate position between decane and dipentene.

The addition of an extra vinyl group to benzene leads to an enhanced interaction with the nitrile rubbers, whereas the introduction of aliphatic groups—which is equivalent to a dilution of the polarizable benzene group—leads to a distinct decrease in swelling of the nitrile rubbers, but has little effect on the other elastomers (see Figure 6). There is no essential difference between "dilution" of the aromatic solvent by the introduction of aliphatic groups in

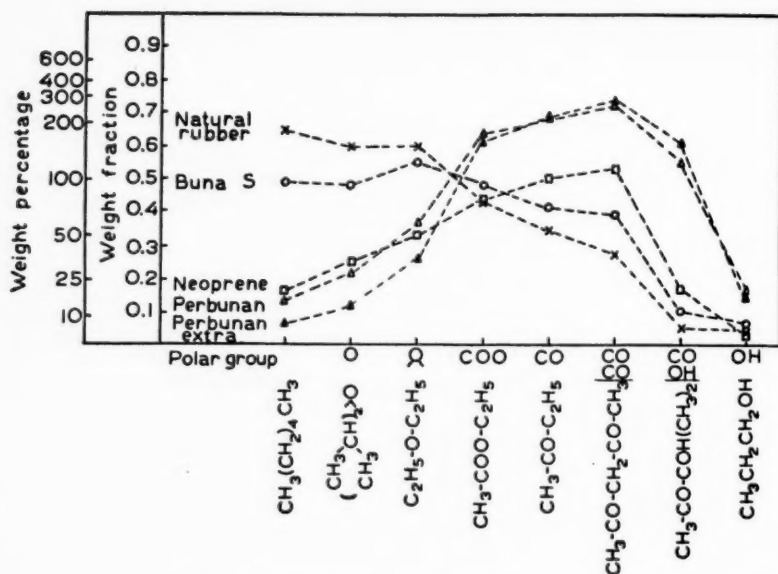


Fig. 4.—Influence of polar groups and hydrogen bonds.

the molecule and dilution with aliphatic hydrocarbons. We measured the change of the swelling equilibrium for such series and found it to be linear with the concentration of aromatics. There are, however, small deviations<sup>15</sup>, *e.g.*, natural rubber swells 320 per cent in benzene, 285 per cent in cyclohexane, and 350 per cent in a mixture of 60 per cent benzene and 40 per cent cyclo-

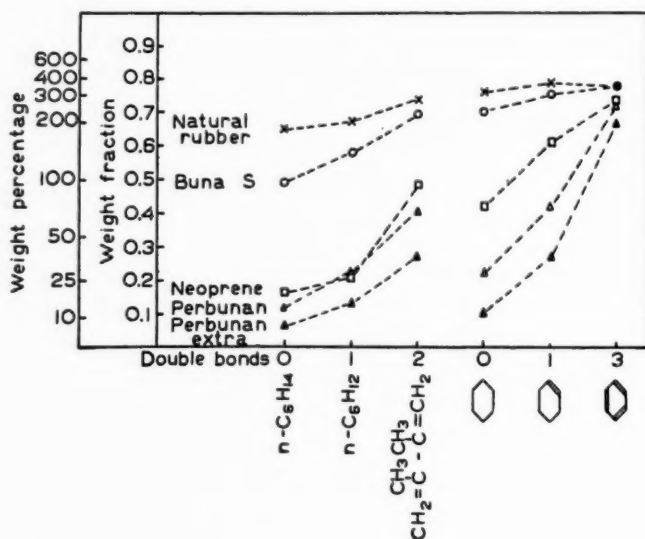
Fig. 5.—Influence of double bond and cyclization on the solvent power of  $\text{C}_6$  hydrocarbons.

TABLE IV  
INFLUENCE OF CYCLIZATION AND DOUBLE BONDS ON SOLVENT POWER  
OF C<sub>10</sub> HYDROCARBONS

Solvent	Swelling, weight fraction				
	Natural rubber	Buna-S	Neoprene	Perbunan	Perbunan-Extra
Tetralin	0.82	0.80	0.78	0.69	0.58
Dicyclopentadiene	0.81	0.79	0.74	0.58	0.42
Dipentene	0.77	0.73	0.61	0.36	0.22
Decalin	0.80	0.74	0.56	0.26	0.09
n-Decane	0.70	0.63	0.33	0.22	0.13

hexane. The enhanced solvent power of mixtures is also a well-known phenomenon for cellulose derivatives.

A comparison of Figures 3 and 7 leads to an interesting result. The influence of polar groups on the swelling power of benzene runs parallel to the effect of polar groups introduced in aliphatic hydrocarbons, but the activity of the polar group in the solvents is in certain cases influenced by the benzene nucleus. As a consequence, nitrobenzene and benzonitrile interact strongly even with natural rubber.

The association of aniline seems to be comparable with that of benzyl alcohol, which would indicate the presence of hydrogen bonds. Further evidence for this assumption can be obtained from a comparison with the *N*-methylated anilines, given in Table V. The latter are better solvents for natural rubber and weaker solvents for the nitrile rubbers. Further data compiled in Table V illustrate the polar nature of some other organic bases. The solvent power of piperidine is quite comparable with that of benzene. Since piperidine is a solvent even for polyisobutylene, it cannot be associated at all. On the other hand, piperidine interacts with the nitrile rubbers, indicating its polarizability. The action of pyridine and quinoline, which have dipole moments of 2.1 and 2.25 debyes, respectively, is quite different. They

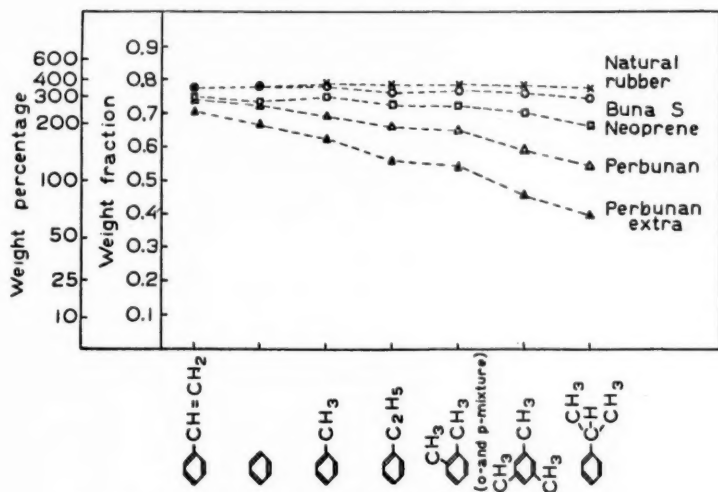


Fig. 6.—Influence of vinyl and aliphatic groups on the solvent power of benzene.

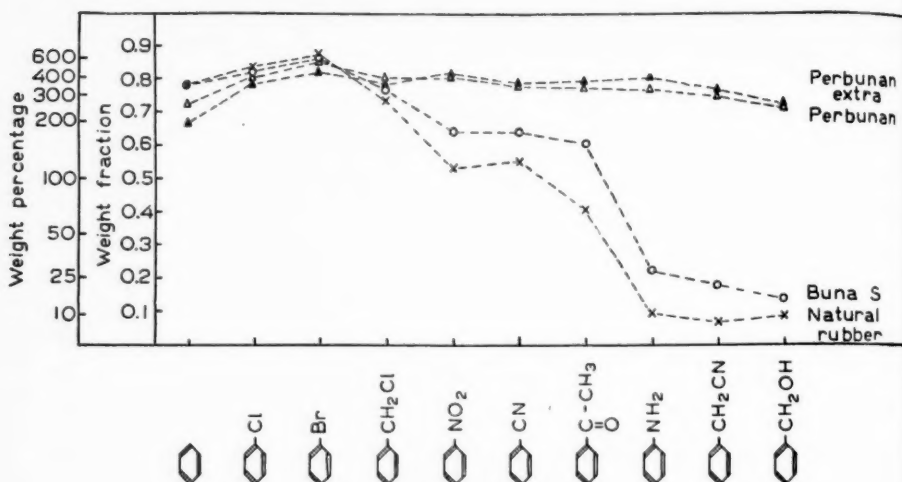


Fig. 7.—Influence of polar groups on the solvent power of benzene.

are sufficiently associated to become a nonsolvent for Oppanol, and they interact strongly with the nitrile rubbers. It should be mentioned that, at the boiling point of quinoline, Oppanol becomes soluble in the base. A comparison of the change in solvent power of six-membered rings, taking cyclohexane as a standard, is given in Figure 8.

The monohalides are sufficiently weakly associated liquids to swell natural rubber, but they interact as well with the nitrile rubbers, which indicates their polarizability. This is also illustrated in some detail by Table VI. In most cases the interaction with Buna-S is more pronounced than with the nitriles; the association of the latter, therefore, cannot be overcome completely by the monohalides.

The solvent power of polyhalides and related compounds, *e.g.*, carbon disulfide, can be understood by taking into account the asymmetrical charge distribution on the molecular surface. In the case of a symmetrical molecule, such as carbon tetrachloride, a distortion of symmetry takes place under the influence of an interacting polar group. The results are given for the methane series in Figure 9 and for the ethane series in Figure 10. The mono-, di-, and trihalides approximate the chloroform type of solvent. Carbon tetrachloride and carbon disulfide, with symmetrical molecules, exhibit distinctly smaller

TABLE V  
SOLVENT POWER OF SOME ORGANIC BASES

Solvent	Swelling, weight fraction					
	Oppanol	Natural rubber	Buna-S	Neoprene	Perbunan	Perbunan-Extra
Piperidine	1.00	0.77	0.80	0.89	0.74	0.69
Pyridine	0.00	0.52	0.67	0.84	0.79	0.80
Quinoline	0.00	0.50	0.69	0.86	0.79	0.81
Dimethylaniline			0.75			0.76
Monomethylaniline			0.60			0.80
Aniline		0.09	0.22		0.77	0.80



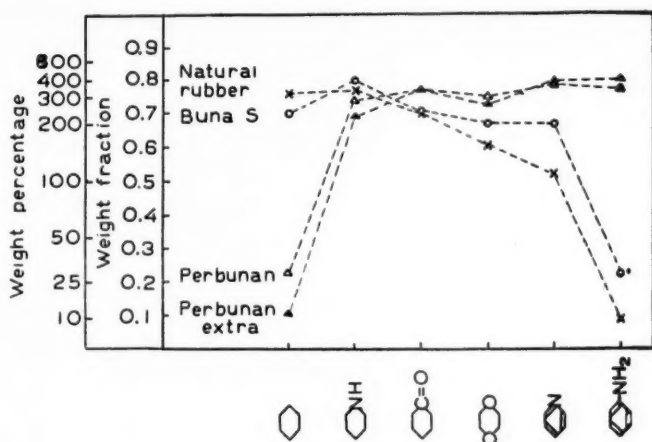


FIG. 8.—Swelling power of six-membered ring compounds.

interaction with the nitrile rubbers, which places their solvent power between that of aromatic and cycloparaffin compounds. Most of the ethane halides apparently belong to the chloroform type since they interact strongly with nitrile rubbers. This is rather surprising because tetrachloroethane is built symmetrically. However, both halves of the molecule having the chloroform structure can rotate freely along the connecting bond, leading to asymmetry. The solvent power of tetrachloroethylene, on the other hand, corresponds to the carbon tetrachloride type, which is probably due to the fact that the two halves of the molecule are fixed by the double bond in the symmetrical position.

#### INFLUENCE OF TEMPERATURE

Although little doubt remains that a swollen gel reaches a true equilibrium with the solvent, a change in temperature should provide direct proof. The results of an extensive experiment with Perbunan are reproduced in Figure 11. Two samples of the rubber were immersed in toluene at 20° and 60° C and the equilibrium, which differed only by 17 per cent in weight, was observed for two days. The samples were exchanged, and reached the reversed equilibrium

TABLE VI  
INFLUENCE OF MOLECULAR STRUCTURE ON SOLVENT POWER OF MONOHALIDES

Carbon atoms	Solvent	Swelling, weight fraction		
		Buna-S	Perbunan	Perbunan-Extra
C <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	0.72	0.70	0.65
	(CH <sub>3</sub> ) <sub>2</sub> CHCl	0.64	0.64	0.56
	CH <sub>2</sub> =CHCH <sub>2</sub> Cl	0.73	0.75	0.72
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br	0.83	0.81	0.72
	(CH <sub>3</sub> ) <sub>2</sub> CHBr	0.80	0.78	0.74
C <sub>4</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	0.72	0.68	0.60
	CH <sub>2</sub> C(CH <sub>3</sub> )CH <sub>2</sub> Cl	0.74	0.73	0.70
	CH <sub>3</sub> CH <sub>2</sub> CHClCH <sub>3</sub>	0.73	0.75	0.72
	(CH <sub>3</sub> )CHCH <sub>2</sub> CH <sub>2</sub> Cl	0.54	0.62	0.50
C <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> Br	0.79	0.73	0.63

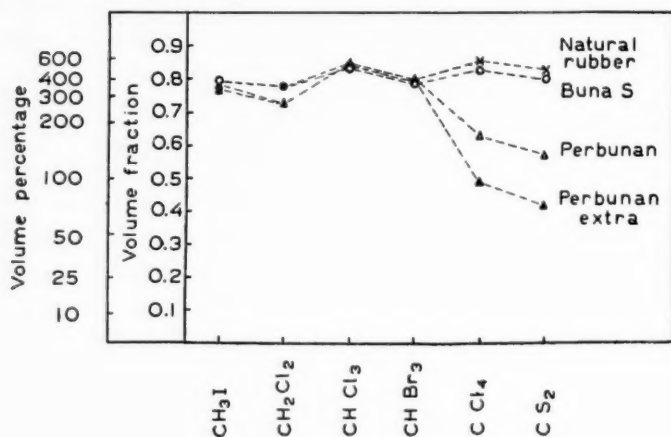


Fig. 9.—Solvent power of methyl halides.

after a few hours. The new equilibrium remained constant for five days, after which the samples were again exchanged and the equilibrium reached almost the old value, the small difference being due to aging. The measured differences correspond only to a change in the weight fractions, by 0.02, but it is evident from Figure 11 that swelling near the equilibrium decreases with an increase in temperature.

The results of some further experiments are summarized in Figure 12. Experiments with natural rubber are less accurate, because of the influence of oxidation during the experiment. The result obtained is surprising in that the temperature has only little influence on the degree of swelling. In some other experiments it was found that the system, Buna-S-carbon tetrachloride and Perbunan-carbon tetrachloride, showed a decrease in swelling at higher

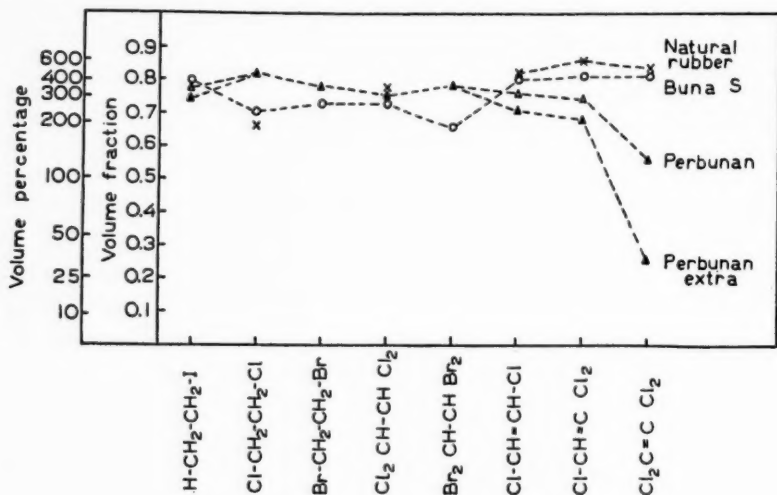


Fig. 10.—Solvent power of ethane and ethene polyhalides.

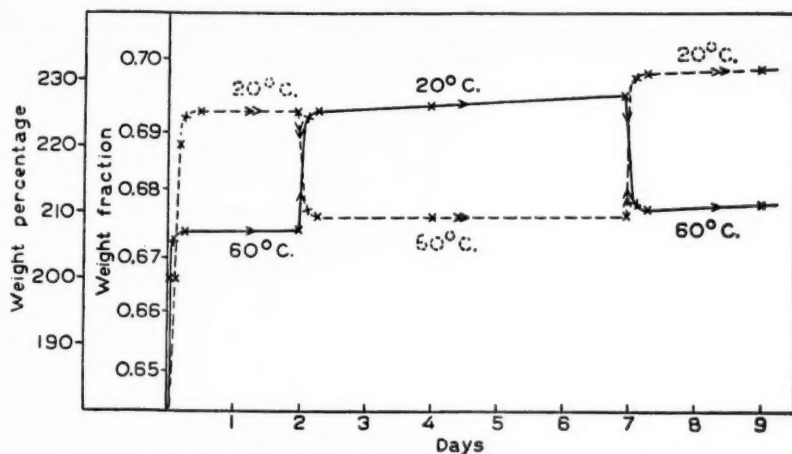


Fig. 11.—Influence of temperature on the swelling equilibrium of Perbunan in toluene.

temperatures, whereas natural rubber and Perbunan with alcohols (amyl and benzyl alcohols) showed a comparatively strong increase in swelling. Apparently, a low degree of swelling has a positive temperature coefficient and a high degree of swelling has a minor negative or no temperature coefficient. The maximum degree of swelling reached for the same elastomer in one solvent, *e.g.*, chloroform, cannot be approached in weaker solvents by an increase in temperature. It is evident that the indifference of moderately swollen elastomers to increased thermal agitation of the solvent molecules cannot be interpreted in terms of liquid-polymer interaction alone; the kinetic counter-pressure of the only partly expanded network must obviously be taken into consideration.

#### EXTERNAL PRESSURE AND MECHANICAL STRAIN

Since the influence of temperature on the equilibrium gave a rather complex picture, we hoped to learn more from an application of strain to the swollen gel.

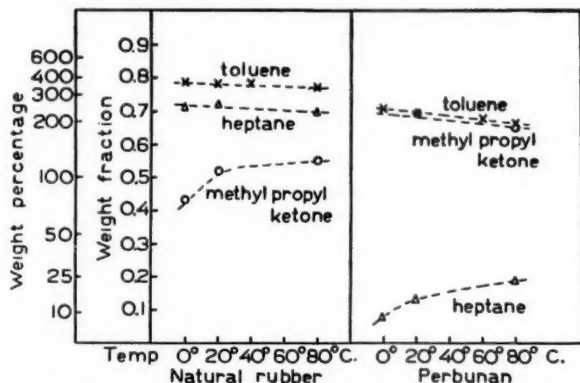


Fig. 12.—Influence of temperature on a series of swelling equilibria.

Before dealing with our results, reference should be made to the much-quoted experiments of Posnjak<sup>16</sup> on the influence of one-sided pressure. The comparison made in Table VII gives a relative measure of the small energetic changes

TABLE VII  
COMPARISON OF SWELLING OF RAW RUBBER UNDER PRESSURE  
WITH SWELLING OF A VULCANIZATE

Solvent	Swelling (weight fraction)	
	Raw rubber under 1.08 atm. pressure	Natural rubber vulcanizate
Chloroform	0.90	0.88
Carbon tetrachloride	0.92	0.90
Ethyl ether	0.70 <sub>s</sub>	0.60
Benzene	0.81 <sub>s</sub>	0.78
Toluene	0.82	0.79
Dichloroethane	0.73	0.71

involved in sol-gel transformation. One atmosphere of pressure applied to a gel of raw rubber is sufficient to reduce the degree of swelling to that of a fully vulcanized rubber at ordinary pressure. One-sided strain should produce similar changes in the equilibrium but, unfortunately, the mechanical properties of gels derived from elastomers interfere with such experiments.

Technical elastomers cannot take up 50–100 per cent softeners or solvents without losing their mechanical strength. In fact, many low-boiling non-solvents, such as alcohols, weaken the strength of stretched elastomers considerably. Moderately swollen systems, *e.g.*, natural rubber-hexane, cannot be kept stretched more than 100 per cent for several days. The following data were obtained from rings of a pure gum mixture in hexane:

Swelling at 25° before extension	189 ± 3%
Extended 100% (40% calculated on the swollen rubber)	211 ± 3%
After release of tension	189 ± 3%
Increase in swelling under extension	+22 ± 6%

These values were obtained by two different methods: (1) stretching the rubber, followed by swelling to a constant value; and (2) swelling the ring to a constant value, followed by stretching the swollen rubber.

By using carbon black mixtures of natural rubber, and chloroform as solvent, the following figures were obtained:

Swelling at 25° before extension	430%
Extended 100% (30% calculated on the swollen rubber)	480%
After contraction	460%
Increase in swelling under extension	+20–50%

It is evident that the small increase in swelling, about 5–10 per cent of the original value, within the very limited range of extensibility, is of too little significance to be correlated to the kinetic properties of the network.

#### SOL-GEL TRANSFORMATION AND CROSS-LINKING

Some additional experiments were performed to compare gels from vulcanized rubbers with sols at one end and ebonites at the other end of the scale. A 1 per cent solution of the elastomer in toluene was prepared, and the quantity of a nonsolvent necessary to produce turbidity was measured. The absolute value of such data is, of course, meaningless unless fractions of constant

molecular weight are used. The following conclusions can be drawn from a relative comparison alone. The nonsolvent activity of the alcohols is of the expected order. It is governed by the quantity of hydroxyl groups per volume and also by the strength of interaction between hydroxyl groups and polymers. The solvent power of ketones also corresponds well with the swelling action on vulcanized elastomers, as can be seen from a comparison of Table VIII and

TABLE VIII  
PRECIPITATION POWER OF LIQUIDS ON 1% SOLUTION OF  
ELASTOMERS IN TOLUENE

Liquid	Volume fraction				
	Oppanol	Natural rubber	Buna-S	Neoprene	Perbunan
Methyl alcohol	0.05	0.12	0.12	0.14	0.33
Ethyl alcohol	0.10	0.19	0.19	0.19	0.40
Butyl alcohol	0.14	0.38	0.31	0.27	0.43
Amyl alcohol	0.23	0.41	0.34	0.27	0.47
Acetone	0.08	0.37	0.43	0.62	sol.
Methylethyl ketone	0.12	0.70	0.74		
Decalin	sol.	sol.	sol.	sol.	0.48
Cyclohexane	sol.	sol.	sol.	sol.	0.35
Hexane	sol.	sol.	sol.	0.40	0.20

Figure 2. The paraffinic hydrocarbons are nonsolvents for raw nitrile rubbers, as has already been discussed in another paper<sup>17</sup>. The precipitation power of hydrocarbons on solutions of Neoprene is less pronounced than on the nitrile rubbers, as could be expected. It is, however, surprising that cyclohexane becomes a solvent for Neoprene in the presence of a small quantity of toluene, whereas the vulcanized samples swell only to a weight fraction of 0.4 in cyclohexane. Weakly vulcanized samples of Neoprene in decalin show a marked increase of swelling on heating, although fully vulcanized samples do not. This indicates that the interaction of polar groups may become fixed by cross-linking in such a way that the association between parts of the macromolecules cannot be separated any more by thermal agitation of the solvent alone. The same number of cross-links in a polar rubber may have a different effect on the swelling equilibrium than in an apolar elastomer.

The vulcanization of natural rubber and Neoprene leads to a fairly constant degree of swelling, independent of the method of vulcanization. On the other hand, the swelling of elastomers from butadiene decreases after aging, a change which can be interpreted as a small increase in cross-links. However, this reduction of swelling by aging is not significant compared with the pronounced decrease in mechanical quality. Large changes in swelling properties can be reached only by transforming the materials to ebonites (Table IX).

TABLE IX  
SWELLING OF HARD RUBBERS\* IN CHLOROFORM AT 25° C

Rubbert	Swelling (weight fraction)
Natural rubber	0.59
Buna-S	0.47
Perbunan	0.49
Perbunan-Extra	0.48

\* Swelling of soft elastomers, 0.88.

† Vulcanization at 147° for three hours: rubber, 100 parts; Vulkacit-CT, 1 part; sulfur, 50 parts; combined sulfur, 30-31%.

Since chloroform interacts strongly with both nitrile groups and sulfur groups, the decrease in swelling can be taken as a direct measure of an increased number of cross-links, which is more pronounced for the synthetic rubbers (decrease, 0.40) than for natural rubber (decrease, 0.29). Further preliminary experiments showed that ebonites from the Perbunans increase in cross-linking with prolonged heating, whereas ebonite from natural rubber reaches a constant value. The gradual formation of the latter can be seen from Figure 13.

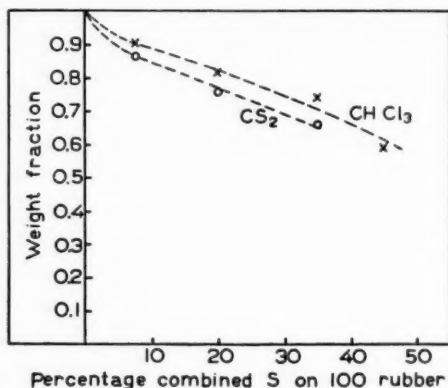


Fig. 13.—Swelling of sulfur derivatives from natural rubber.

It is evident that the network of ebonite is quite comparable to that of natural rubber, so that the higher temperature of elasticity is due mainly to the polar sulfur groups.

#### ABSOLUTE VALUE OF SWELLING EQUILIBRIUM

We have found empirically that the maximum degree of swelling can be reached in chloroform and is similar for all elastomers. How closely this value approaches that of a fully extended network cannot be estimated, since no independent methods exist for evaluating the elastic counterpressure of the gel. The great influence of pressure on the position of the equilibrium indicates that the absolute value is very sensitive to minute energetic changes. Keeping a network of constant dimensions in mind one can deduce from our experiments the following correlations for liquid-solvent interaction which can cause a reduction in swelling: (1) association within the polymer insufficiently compensated by liquid-polymer interaction, and (2) association within the liquid insufficiently compensated by liquid-polymer interaction.

Since the strength of interaction depends on the mutual attraction of both components, swelling can scarcely be correlated with only one physical property of the original components. The relative swelling power, however, of a liquid can be easily evaluated by placing it in one of the following four series: (1) an homologous aliphatic series; (2) a series of polarizable or polar groups of increasing strength attached to either an aliphatic, cyclic, or aromatic group of constant size; (3) a series of hydrocarbons of similar molecular weight changing from aliphatic to olefinic, hydroaromatic, and aromatic compounds; and (4) a series of polyhalides of increasing asymmetrical distribution of charges on the molecular surface.



Finally, it should be mentioned that the rate of diffusion during the swelling process of polyisobutene is distinctly lower than that for unsaturated elastomers. This phenomenon is parallel with the low permeability to gases<sup>18</sup> and can probably be explained by the strong intermolecular attraction between the methyl groups of the flow unit. The solubility of gases in elastomers is also correlated with the swelling of elastomers in liquids. In both cases polarity and polarizability of the two components are of great importance for the absolute value of equilibrium. However, in comparing different gases, the volatility of the gas, for which its critical temperature is a measure, is of far greater significance than its polar or polarizable character—which is in contrast to the behavior of liquids.

#### ACKNOWLEDGMENT

The authors wish to thank the Rubber Foundation for permission for publication, A. Timmer for his assistance in carrying out the laboratory experiments, and C. Koningsberger for frequent discussions.

#### REFERENCES

- <sup>1</sup> Hildebrand, "Solubility of Nonelectrolytes", Reinhold Publishing Co., New York, 1936. For a general discussion on structure and molecular forces in pure liquids and solutions, see *Trans. Faraday Soc.* **33**, 1 (1937).
- <sup>2</sup> Gee, in "Advances in Colloid Science", edited by Mark and Whithy, Interscience Publishers, Inc., New York, 1946, Vol. 2, p. 145.
- <sup>3</sup> Meyer, "Hochpolymere Chemie", Becker and Erler, Leipzig, 1940, Vol. 2, p. 549.
- <sup>4</sup> Gee, *Trans. Faraday Soc.* **38**, 418 (1942); *Trans. Inst. Rubber Ind.* **18**, 266 (1943).
- <sup>5</sup> Van Laar and Hildebrand, "Solubility of Nonelectrolytes", Reinhold Publishing Co., New York, 1936, p. 73.
- <sup>6</sup> Ferry, Gee and Treloar, *Trans. Faraday Soc.* **41**, 360 (1945).
- <sup>7</sup> Van Amerongen, *J. Applied Physics* **17**, 972 (1946).
- <sup>8</sup> See Staverman, *Rec. trav. chim.* **60**, 827 (1941); *Chem. Weekblad* **35**, 772 (1938).
- <sup>9</sup> Landolt-Börnstein, "Physikalisch-chemische Tabellen", Julius Springer, Berlin, 1923, Vol. 2.
- <sup>10</sup> Schulz, *Z. physik. Chem.* **A179**, 332 (1937).
- <sup>11</sup> Frenkel, *RUBBER CHEM. TECH.* **13**, 264 (1940).
- <sup>12</sup> Whithy, Evans and Pasternack, *Trans. Faraday Soc.* **38**, 269 (1942).
- <sup>13</sup> Scott, *Trans. Inst. Rubber Ind.* **5**, 95 (1929).
- <sup>14</sup> Wolf and Lederle, *Physik-Z.* **29**, 948 (1928); Wolf, *Z. physik. Chem.* **B2**, 39 (1929).
- <sup>15</sup> See also Gee, *Trans. Faraday Soc.* **40**, 477 (1944).
- <sup>16</sup> Posnjak, *Kolloidchem.-Beih.* **3**, 417 (1912).
- <sup>17</sup> Koningsberger and Salomon, *J. Polymer Science* **1**, 353 (1946).
- <sup>18</sup> Van Amerongen, *J. Applied Physics* **17**, 972 (1946).

# HEAT CONDUCTION AND MOLECULAR STRUCTURE IN RUBBERLIKE POLYMERS \*

JOHN REHNER, JR.

ESSO LABORATORIES, STANDARD OIL DEVELOPMENT COMPANY, ELIZABETH, NEW JERSEY

## INTRODUCTION

The capacity of rubber compositions to conduct heat is an important factor in the processing and vulcanization of rubber stocks. For this reason a number of investigations have been made<sup>1</sup> of heat conduction in natural rubber and some of its compounding ingredients. In general, the thermal conductivity has been found to be the sum of the conductivities of the components present in the mixture, multiplied by their relative volume concentrations. Also, the state of cure is without any apparent influence since the values for cured and uncured compositions are alike within the limits of experimental error.

Published data on thermal conductivity in synthetic rubbers are quite limited. A few values have been reported by Jacobi<sup>2</sup>, but the compositions of the stocks were not disclosed. Houwink<sup>3</sup> also has tabulated some values, but does not cite the origins of much of the data, nor does he report the experimental methods employed and the temperatures of the measurements. Also, the compositions are not well defined; for example, it is not known whether the vulcanizates contained plasticizers or softeners. Somewhat earlier, Frumkin and Dubinker<sup>4</sup> published data for both natural and "synthetic" rubber stocks. The latter were not identified, but were presumably made with butadiene polymers. Their results, furthermore, cannot be accepted as reliable, for in their treatment of the data these investigators made a fairly common mistake that can lead to large errors, as will be discussed.

Aside from practical considerations, it has been recognized<sup>5</sup> that no molecular physical theory of thermal conductivity exists at the present time. In the course of obtaining systematic data to serve toward this end, we have found that an analysis of the problem gives rise to some aspects of more general, and hitherto presumably unrelated, interest in the field of high polymer behavior. These will be discussed later.

## EXPERIMENTAL

### MATERIALS

The natural rubber used in this work was a sample of ribbed smoked sheet. The Butyl rubber was a copolymer of isobutylene and isoprene known as GR-I, containing about 1 per cent of isoprene units. Perbunan-18, Perbunan-26, and Perbunan-35 were emulsion copolymers of butadiene and acrylonitrile; the numbers designate the percentage by weight of acrylonitrile units in the copolymer. The Buna-S was an emulsion copolymer of butadiene and styrene known as GR-S, containing about 25 per cent of styrene units. The polybutadiene and polyisoprene were emulsion polymers. The polychloroprene

\* Reprinted from the *Journal of Polymer Science*, Vol. 2, No. 3, pages 263-274, June 1947.

was a commercial sample of Neoprene-GN. The dimethylsiloxane polymers were commercial samples of Silastic-160 and Silastic-180. Bardol, a commercial tar distillate, was the softener, and Kosmobile-66 was the carbon black employed in some of the recipes. The other compounding ingredients were of regular rubber grades.

The following formulas and vulcanizing conditions were used in preparing the pure-gum compositions (numbers in parentheses represent parts by weight).

- (1) Smoked sheet (100), zinc oxide (5), stearic acid (1), benzothiazoyl disulfide (1), sulfur (2). Cured 60 minutes at 287° F.
- (2) GR-I (100), zinc oxide (5), stearic acid (1), tetramethylthiuram disulfide (1), sulfur (2). Cured 60 minutes at 307° F.
- (3) Perbunan-18 (100), other ingredients and cure as in Formula 1.
- (4) Perbunan-26 (100), other ingredients and cure as in Formula 1.
- (5) Perbunan-35 (100), other ingredients and cure as in Formula 1.
- (6) GR-S (100), zinc oxide (5), stearic acid (1), mercaptobenzothiazole (1), sulfur (2). Cured 60 minutes at 287° F.
- (7) Polybutadiene (100), other ingredients and cure as in Formula 6.
- (8) Polyisoprene (100), other ingredients as in Formula 6. Cured 30 minutes at 210° F, followed by 60 minutes at 270–320° F.
- (9) Neoprene-GN (100), zinc oxide (5), magnesia (4). Cured 30 minutes at 287° F.
- (10) Silastic-160. Molded 5 minutes at 250° F, and cured overnight in an air oven at 450° F.
- (11) Silastic-180. Same molding and curing treatment as in Formula 10.

Stocks containing 20 parts of Bardol, but without stearic acid, were prepared with the formulas and vulcanizing conditions given in Formulas 1 to 5, inclusive. These are designated as 12 to 16, respectively.

Stocks 17 to 21 were prepared with the same formulas and vulcanizing conditions as 12 to 16, respectively, but contained in addition 54 parts of carbon black.

#### METHOD

Rubber spheres were prepared by vulcanizing the various stocks in a mold having a cavity diameter of about 2 inches. Each sphere was then frozen in dry ice and cut into two hemispheres by means of a band saw. The junction of a fine (0.01-inch) calibrated copper-constantan thermocouple was carefully located at the center, and the hemispheres were cemented together with a fast-curing rubber cement and held with a clamp. The assembly was heated overnight at 70° C to cure the bond. Since the sawing resulted in a slight asymmetry, the radius of the sphere was taken as the average of several measurements. This was found to be 2.50 cm. at room temperature. The increase in diameter (from 1.0 to 1.7 per cent, depending on the stock) on subsequent immersion in boiling water was neglected.

The specimen was brought to a uniform temperature by overnight immersion in a water bath maintained near  $25 \pm 0.2^\circ \text{C}$ . The thermocouple leads were then connected to a Leeds and Northrup precision potentiometer (the cold junction being kept in an ice-water mixture), and the initial temperature at the center of the sphere was measured. The sphere was then quickly removed from the water bath and plunged into a large beaker of vigorously boiling distilled water. Specimens having a low specific gravity were kept submerged by

means of a frame, making three-point contacts with the specimen. Temperature readings were taken to within  $0.02^\circ\text{C}$  at 4- or 5-minute intervals for a period of about one hour. The barometric pressure was taken before and after the run, and was used to establish the boiling point of the water.

For each stock parallel measurements were made with either the same or a duplicate specimen to determine the reproducibility of the results. Measurements were also carried out in each case with a sphere that had been allowed to reach its initial uniform temperature in a closed empty Dewar flask, so as to insure that overnight exposure in contact with water did not influence the results.

#### TREATMENT OF DATA

The experimental method described above consists in determining the temperatures,  $T_c$ , at various times,  $t$ , at the center of a sphere which was initially at a uniform temperature,  $T_0$ , and was then suddenly plunged into a constant-temperature bath which maintained the surface temperature,  $T_1$ , constant. The solution of the Fourier heat equation for the boundary conditions:

$$T = T_0 \quad \text{when} \quad t = 0 \quad (1)$$

$$T = T_1 \quad \text{when} \quad r = a \quad (2)$$

for a sphere of radius  $a$ , has been given by Byerly<sup>6</sup> and can be written:

$$u_c = \frac{T_1 - T_c}{T_1 - T_0} = 2 \sum_{m=1}^{m=\infty} (-1)^{m+1} \exp(-m^2\pi^2kt/a^2) \quad (3)$$

The solution of Equation (3) for  $k$  is carried out most easily with the aid of graphs prepared by Williamson and Adams<sup>7</sup>. Before describing the application of Equation (3) and the method devised to take into account, as well as to determine, the temperature dependence of  $k$ , it is relevant to discuss at this point the work of Frumkin and Dubinker<sup>4</sup> referred to above.

These investigators allowed their rubber spheres to come to a uniform temperature and then placed them in an air chamber kept at constant temperature. Under these conditions the surface temperature can no longer be simply expressed, and the boundary conditions are now given by:

$$T = T_0 \quad \text{when} \quad t = 0 \quad (4)$$

$$dT/dr = h(T_1 - T) \quad \text{when} \quad r = a \quad (5)$$

That is, radiation from the solid surface into the surrounding gas takes place with a continuously changing surface temperature and at a rate which depends on the emissivity,  $h$ ; the latter is known to depend on the state of the solid surface and temperature, so in experimental work it is best to reduce radiation losses to the magnitude of a small correction, either by treating the surface with a suitable material or by using a liquid bath with good contact and conductivity superior to that of a gas<sup>8</sup>. The general solution of the heat equation under conditions (4) and (5) has been given by Byerly<sup>9</sup>. Developing this solution for the limit  $r = 0$ , that is, for the temperature at the center of the sphere, and evaluating the integral for the case of a sphere which is initially at a uniform temperature, we find that:

$$\frac{T_1 - T_c}{T_1 - T_0} = 2 \sum_{m=1}^{m=\infty} a_m b'_m \exp(-a_m^2 kt) \quad (6)$$

where  $a_m$  is a root of:

$$ax \cos ax + (ha - 1) \sin ax = 0 \quad (7)$$

and

$$b'_m = \frac{a_m^2 a^2 + (ha - 1)^2}{a_m^2 a^2 + (ha - 1)ha} \frac{1}{a_m} \left\{ 1 - \cos a_m a + \frac{1}{a_m a} \sin a_m a \right\} \quad (8)$$

It is seen that Equation (6) differs considerably from Equation (3), and depends on  $h$  in a complicated manner.

While Frumkin and Dubinker used the graphical equivalent<sup>7</sup> of Equation (3) in computing their results, their experimental conditions conformed to Equation (6); in other words, while their experiments did not preclude emissivity as an important factor, they did not take the latter into account in analyzing the data. Since the emissivities of their rubber stocks are not known, the magnitude of the error in their results cannot be determined. That the latter may be large is indicated by the data of Hahn<sup>10</sup> for natural rubber stocks heated in gas-free steam and in air. Hahn estimates emissivities of 0.41 and 0.0016 c.g.s. units, respectively, in these media. It is likely that comparably great differences would be found with synthetic rubbers.

For each observed value of the reduced temperature,  $u_c$ , the corresponding value of  $kt/a^2$  was taken from a photographic enlargement of the curve of Williamson and Adams showing the variation of  $u_c$  with  $kt/a^2$  for a sphere subjected to sudden warming. Since the values of  $a$  and  $t$  were known,  $k$  was thus determined. Data corresponding to the early and late intervals of each run, for which  $u_c$  was found to be greater than 0.9 or less than 0.1, were either disregarded or given less weight in the plots, for in these intervals the graphical values of  $kt/a^2$  could not be read accurately.

#### MEAN TEMPERATURE OF A SPHERE ON SUDDEN WARMING

As the experiment progresses, the central temperature steadily increases from its initial value and approaches that of the hot water bath. The series of values of  $k$  determined by the foregoing procedure thus corresponds to a steadily increasing mean temperature of the sphere. Definition of the latter has proved to be elusive; for while the need for plotting  $k$  against some mean temperature of the sphere has been recognized<sup>4</sup>, the dependence of the temperature within the sphere on both time and radial distance from the center limits the value of plots<sup>4</sup> of  $k$  vs.  $T_c$  or vs.  $(T_c + T_1)/2$ , which are highly conditional and of restricted utility when applied to nonspherical cases. This difficulty can be circumvented in the following manner.

Williamson and Adams<sup>7</sup> give curves showing that the reduced temperature,  $u$ , varies with the distance from the center of the sphere for different values of  $kt/a^2$ . By integrating the area under each of these curves planimetrically and plotting the resulting "diffusivity-average" reduced temperature  $u_{AV}$  as a function of  $kt/a^2$ , the curve shown in Figure 1 was obtained. By means of this curve, the value of  $u_{AV}$  corresponding to each measured value of  $kt/a^2$  was determined, and from this the diffusivity-average temperature,  $T_{AV}$ , of the sphere at each instant of measurement was computed.

It was found that  $T_{AV} < (T_c + T_1)/2$ , and that the difference is greatest at the lowest temperatures, ranging from 5° to 22° C as  $T_c$  decreases from the highest value employed (about 88°) to the lowest value employed (about 37°). The importance of such differences is obvious in instances where it is necessary to extrapolate values of  $k$  to higher or lower temperatures.

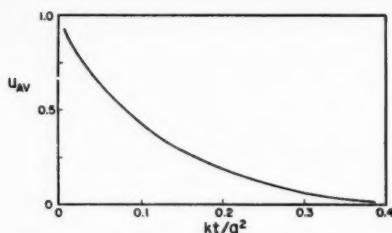


FIG. 1.—Dependence of "diffusivity-average" reduced temperature on  $kt/a^2$  for a sphere subjected to sudden warming or cooling.

## RESULTS

A typical set of results is given in Figure 2, in which  $k$  is shown as a function of  $T_{AV}$  for a natural rubber vulcanizate. As a rule, spheres that had been conditioned by water immersion gave more reproducible results and less scattering than did those conditioned in an empty Dewar flask. This may be due to a wetting effect, in which a surface film of gas or other poorly conducting material is displaced by a water layer, resulting in improved emissivity. Taking experimental and analytical errors into account, values of  $k$  read from the graph are probably accurate within about 5 per cent, while the slope or temperature coefficient of  $k$  is probably reliable to within 10 per cent.

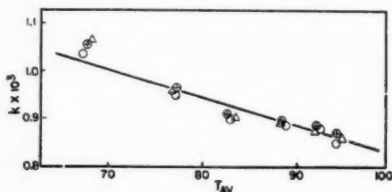


FIG. 2.—Dependence of thermal diffusivity on temperature for natural rubber. The open and crossed circles refer to specimens conditioned in water, and the triangles to a sphere conditioned in an empty Dewar flask.

Results for the various rubber stocks are given in Table I, in which the values of  $k$ , listed for temperatures of 60° and 140° C as a matter of convenience, were obtained by linear extrapolation of plots similar to Figure 2. The main features of the experimental results may be briefly summarized as follows. (1) The thermal diffusivity of rubberlike polymers decreases linearly with increasing temperature, at least over the range investigated. Since the thermal conductivity of rubber increases with temperature, closely paralleling the specific heat and specific volume curves over a wide temperature range<sup>11</sup>, the negative temperature coefficient of  $k$  indicates that, for each of the rubbers considered here, the product of the density and the specific heat increases more rapidly with increasing temperature than does the thermal conductivity. (2) The value of  $k$  at a given temperature depends appreciably, but not greatly, on the nature of the polymer. (3) For a given polymer and temperature,  $k$  is least in pure-gum stocks and greatest in carbon-black stocks. Addition of 20 parts of Bardol decreases  $k$  by  $0.03 \pm 0.01 \times 10^{-3}$  at 60° C, and by  $0.05 \pm 0.01 \times 10^{-3}$  at 140°, while 54 parts of the carbon black increases  $k$  by  $0.46 \pm 0.01 \times 10^{-3}$  at 60° and by  $0.32 \pm 0.01 \times 10^{-3}$  at 140° C. The practi-



TABLE I  
EXTRAPOLATED VALUES OF THERMAL DIFFUSIVITY  
FOR VARIOUS SYNTHETIC RUBBERS

Rubber	Formula	Type of stock	$k \times 10^3$ , cm. <sup>2</sup> /sec.		$\frac{\Delta k}{\Delta T} \times 10^3$ , per °C
			60° C	140° C	
Natural rubber	1	Pure gum	1.06	0.59	0.59
Butyl (GR-I)	2		0.89	0.51	0.48
Perbunan-18	3		1.19	0.78	0.51
Perbunan-26	4		1.21	0.79	0.53
Perbunan-35	5		1.21	0.80	0.51
Buna-S (GR-S)	6		1.24	0.57	0.84
Polybutadiene	7		1.20	0.73	0.59
Polyisoprene	8		1.13	0.73	0.50
Neoprene-GN	9		1.09	0.65	0.55
Silastic-160*	10		2.88	2.26	0.78
Silastic-180*	11		2.79	2.33	0.58
Natural rubber	12	Pure gum + Bardol	1.05	0.60	0.56
Butyl (GR-I)	13		0.93	0.46	0.59
Perbunan-18	14		1.15	0.73	0.53
Perbunan-26	15		1.14	0.73	0.51
Perbunan-35	16	Bardol + carbon black	1.18	0.72	0.58
Natural rubber	17		1.49	0.92	0.71
Butyl (GR-I)	18		1.34	0.65	0.86
Perbunan-18	19		1.66	1.16	0.63
Perbunan-26	20		1.64	1.10	0.68
Perbunan-35	21		1.63	1.04	0.74

\* This designation of stock type may be incorrect for these polymers, which appear to contain a filler of undisclosed composition and amount.

cally negligible effect of the softener means that  $k$  for a hydrocarbon such as Bardol is comparable in value to that of the polymer, whereas that of carbon black is considerably higher. (4) The temperature coefficients of  $k$  differ by less than twofold for the rubbers investigated. Bardol has a negligible influence on the temperature coefficient, but carbon black increases its absolute value considerably. (5) The thermal diffusivity of Perbunan polymers is independent of the nitrile content, within experimental error, and equal to that of polybutadiene. (6) Substitution of chlorine for the methyl side groups in natural rubber to form polychloroprene has no significant influence on  $k$ . (7) Polyisoprene and natural rubber have nearly the same value of  $k$  at room temperatures, but that of the synthetic polymer is somewhat higher at vulcanization temperatures.

#### HEAT CONDUCTION AND CHEMICAL STRUCTURE

*Rubberlike and liquid states.*—On the basis of general considerations, Müller<sup>12</sup> has suggested that thermal conductivity is related to the strength of the interatomic binding forces, *e.g.*, the high values of the latter in metals are supposed to result in high values of thermal conductivity, while the relatively low values in organic polymers are considered not only to result in correspondingly low thermal conductivities but also in asymmetry. That is, the conductivity along the main valence chain should differ from that between chains, and a highly oriented polymer should, therefore, be anisotropic in this property—although no data seem to be available on this point. Nevertheless, insofar as binding forces are concerned, the polymeric state should resemble that of an organic

liquid, according to Müller's view, rather than the metallic or solid state; and it is known that the conduction of heat in these states of matter agrees, at least roughly, with the suggested pattern.

It has long been recognized that the rubberlike and liquid states have much in common. The similarity arises from various kinds of evidence, such as the similarities of their x-ray diagrams, the readiness with which groups of atoms in neighboring chains can slide past each other (like molecules in a viscous liquid), and the rapid speed of retraction of stretched rubber on release. Also, in the process of melting of crystallites in long-chain polymers, only the linkages transverse to the molecular axis are weakened, so that the links of the chains are free to move as in a liquid. Furthermore, the ease with which the shape of rubber can be changed under the influence of ordinary weak deforming forces, as a consequence of the very low elastic moduli compared with those of solids, is an argument in favor of the similarity to liquids. Such considerations have led to the proposal<sup>13</sup> that rubber molecules be regarded as "solid in one dimension and liquid in the other two dimensions". Expressed in this manner, the concept seems obscure if not meaningless, probably because of the semantic difficulty in attempting to ascribe reality to a fundamentally nonexistent difference between the liquid and solid states for substances whose behavior is dependent on the relationship of their relaxation frequencies to the frequency of the external forces. The crux of the analogy, therefore, lies in determining whether properties of rubberlike substances are describable by laws known to hold for ordinary liquids.

*Thermal conductivity and sound velocity.*—The relationship between thermal conductivity and sound velocity in liquids has been the subject of several theoretical and experimental treatments<sup>14</sup>. Basing his work on the idea that thermal agitation is transmitted by compressional movements with a velocity comparable to that of sound, Bridgman<sup>15</sup> derived a simple formula that agreed within about 15 per cent with experimental values for a variety of liquids. Proceeding from this idea with a somewhat different approach, and introducing certain corrections previously derived by Eucken, Powell, Roseveare, and Eyring derived the following equation:

$$W \text{ (liquid)} = 0.931 (c_V/c_P)^{1/3} 3k_B(N/V)^{1/3}v \quad (9)$$

where  $W$  is the thermal conductivity,  $c_V$  and  $c_P$  are the specific heats,  $k_B$  is the Boltzmann constant,  $N/V$  is the number of molecules per cc. of liquid, and  $v$  is the velocity of sound in the liquid. Equation (9) also gives values in excellent agreement with experiment, and it seems likely that this relationship contains the essential factors determining thermal conductivity in liquid systems.

Boyer and Spencer<sup>16</sup> have brought to attention the difficulty of explaining, on the basis of Bridgman's equation, the sudden drop in the thermal conductivity of rubber in the transition region. Equation (9) appears to be consistent with this behavior, since it contains as factors the specific heats, which are known<sup>11</sup> to undergo a parallel behavior at transition temperatures.

Since Equation (9) appears to be reasonably well established for ordinary liquids, we have attempted to determine its applicability to the rubberlike state. Unfortunately, while  $c_P$  is known for several rubbers, this is not the case with  $c_V$  or  $v$ . The procedure we have therefore adopted is to calculate  $c_V$  for several rubberlike polymers for which suitable data are available, and then to determine whether the values of  $v$  computed from Equation (9) are of the correct order of magnitude.

*Calculation of  $c_V$  for polymers.*—The most complete theory of the heat capacity of high polymers available is contained in two recent papers by Tarassov<sup>17</sup>. Treating the law of distribution of vibration frequencies in one-dimensional continua (linear high polymers) and two-dimensional continua (netted high polymers) in a manner essentially the same as that employed by Debye for crystalline solids, Tarassov showed that at Debye temperatures the vibrational heat capacity at constant volume,  $c_1$ , of a linear polymer is given by:

$$c_1 = \pi^2 R(T/\theta) - 3R/Z \quad (10)$$

while that of a netted polymer,  $c_2$ , is given by:

$$c_2 = 43.27R(T/\theta)^2 \quad (11)$$

where  $R$  is the gas constant,  $T$  is the absolute temperature,  $\theta$  is a characteristic temperature, and  $Z$  is the degree of polymerization. The second term in the right member of Equation (10) can ordinarily be neglected. Thus, in contrast with the familiar  $T^3$  law for crystals,  $c_1$  should be proportional to  $T$  for a linear polymer in the proper temperature range. Specific heat data allow one to determine whether Equation (10) is valid and, if so, to determine  $\theta$ . For a natural polyisoprene chain, in which four carbon atoms of each structural unit are in the main valence chain while the fifth is in a side group, Tarassov has shown that  $c_1$  is determined by the chain carbon vibrations, the side group playing a negligible part. It is assumed that the quantity ( $c_P - c_V$ ) does not change much over the range up to the neighborhood of the transition temperature; then, the slopes of the  $c_1$  and the  $c_P$  curves can be taken as approximately equal. By extrapolating the linear portion of the specific heat curve to absolute zero, a positive intercept is obtained which can be taken as the sum of ( $c_P - c_V$ ) and the specific heat of the rotational vibrations. This enables a correction to be made for the rotational energy included in  $c_P$  at Debye temperatures, and is also in a sense a measure of the flexibility of the polymer chain, as will be discussed below. For further details in carrying out the computation of  $c_V$  the original articles<sup>17</sup> may be consulted.

Examination of the specific heat curves for natural rubber<sup>18</sup>, polyisobutylene<sup>19</sup>, a butadiene-acrylonitrile copolymer (Hycar-OR)<sup>20</sup> and polydimethylbutadiene (Methyl rubber W)<sup>21</sup> shows excellent agreement with Equation (10).

In carrying out the computation of  $c_V$  at, say, room temperatures, it is considered that one completely excited rotational group vibration appears for each chain carbon atom in the structural unit, and a contribution of  $R$  calories per chain atom is then made to  $c_1$ . While this procedure is straightforward with simple polymers, some clarification is necessary in the case of a copolymer, such as Hycar-OR, in which three kinds of structural units appear to be involved; namely, 1,2- and 1,4-butadiene units and acrylonitrile units. From the nitrogen analysis of this polymer (10.2 per cent) and the assumption<sup>22</sup> that roughly 20 per cent of the butadiene units have the 1,2 structure, the "average" monomer unit in the molecule is found to have a molecular weight of 53.7, and to contain nearly three chain carbon atoms.

*Coefficient of compressibility.*—After the values of  $c_V$  were calculated, the coefficient of compressibility,  $\kappa$ , was obtained by means of the thermodynamic relationship:

$$c_P - c_V = \alpha^2 T V_{sp} / \kappa \quad (12)$$

where  $\alpha$  is the coefficient of volume expansion, and  $V_{sp}$  is the specific volume.

We were unable to find values of  $\alpha$  and  $V_{sp}$  in the literature for Methyl rubber W, although data are available for the other polymers studied. We, therefore, used the values  $\alpha = 7.2 \times 10^{-4}$  (average for the range 25–50° C), and the density values of 0.913 and 0.897 for 25° and 50°, respectively, which we determined for a sample of polydimethylbutadiene polymerized at 80° in the presence of ether, with sodium as the catalyst.

*Calculation of the sound velocity.*—By proceeding with the data obtained as described above,  $v$  was computed from Equation (9), employing values of  $W$  obtained by converting appropriate pure gum values of  $k$  in Table I through multiplication by the product of the density and specific heat, and letting  $N/V$  be the number of monomer units per cubic centimeter. The reasonable assumption was made that the values of  $k$  for Butyl rubber and Perbunan-35 are approximately equal to those for polyisobutylene and Hycar-OR, respectively. Also, since the rotational energy correction for polyisobutylene suggested that hindered rotation may persist in this polymer at Debye temperatures, or higher, two values of  $v$  were computed in this case corresponding, respectively, to completely hindered and completely excited rotational freedom.

### DISCUSSION

The values of the various properties derived by the preceding treatment are collected in Table II, which contains several interesting points for discussion. It is noted in the fifth column that the correction for the rotational energy included in  $c_p$  for polyisobutylene at Debye temperatures is practically zero; this indication of strongly hindered rotation or lack of chain flexibility is supported by independent data for this polymer. For example, the large discrepancy between the experimental and theoretical heats of polymerization of isobutylene, as well as the examination of a Fisher-Stuart model of the polymer molecule, indicates great steric hindrance between the methyl groups of successive isobutylene units, as has been pointed out by Rossini<sup>23</sup>. Also light scattering results<sup>24</sup>, for polyisobutylene solutions, can be interpreted on the same basis. The absence, therefore, of a rotational correction is not surprising, especially in view of the lower temperatures from which the extrapolation is made. On the other hand, the corrections for Hycar-OR and natural rubber, since they are roughly equal, suggest that these polymers are quite alike with respect to freedom of rotation. This would mean that the pendent vinyl and nitrile groups in butadiene-nitrile copolymers have rotational properties much the same as those of the methyl groups in natural rubber, in accord with the observation that there is not much difference in size between methyl, vinyl, and nitrile groups. The rotational freedom in polydimethylbutadiene appears to be only slightly less; the difference, if significant, may arise from the contiguity of the two methyl groups in the monomer unit.

The results in the sixth column of Table II show a marked effect of chemical structure on compressibility, which is indicated more clearly in Figure 3. It is seen that, as the amount of methyl substitution along the main valence chain is increased, the compressibility is decreased; thus, polyisobutylene, which contains one methyl group for each chain carbon atom on the average, is four times as incompressible as natural rubber, which contains one methyl group for each four chain carbon atoms. This indicates that repulsion between the substituent groups is intimately related to freedom of rotation or flexibility, as would be expected. The effect of the chemical nature of the side group is evident in the divergence of Hycar-OR, in which the polarity of the nitrile group is apparently important.

TABLE II  
THERMAL AND MECHANICAL PROPERTIES OF RUBBERLIKE POLYMERS

Polymer	Characteristic Debye temperature ( $^{\circ}$ K)	Specific heat at 300 $^{\circ}$ K (cal. per g.)		Specific heat correction for rotation (cal. per g.)	Coefficient of compressibility $\times 10^6$ (sq. cm. per kg.)	Density at 300 $^{\circ}$ K (g. per cc.)	Thermal diffusivity $\times 10^4$ at 300 $^{\circ}$ K (sq. cm. per sec.)	Velocity of sound (meters per sec.)		
		<i>c<sub>p</sub></i>	<i>c<sub>v</sub></i>					From Equation (9)	From mechanics*	Experimental†
Polyisobutylene	500	0.470	0.268	0.00	13.0	0.91	1.1	16,000–19,000‡	2900	
Hycar-OR	1050	0.473	0.360	0.0464	9.6	1.00	1.3	16,600	3230	
Natural rubber	1000	0.452	0.386	0.0406	53.7	0.906	1.2	15,800	1430	37§
Methyl rubber W	650	0.47	0.355	0.039	34.8	0.913				

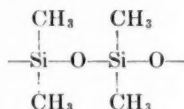
\* For a compression wave in an infinite medium.

† For a longitudinal wave in a finite bar.

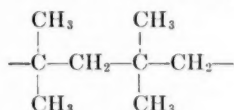
‡ Corresponding to the assumption of completely free and completely hindered rotation, respectively.

§ Exner (*Sitzber. Akad. Wiss. Wien. Math. naturw. Klasse* **69**, IIb, 102 (1874)).

The relatively small, though technologically important, differences between the thermal diffusivities listed in Table I can be readily attributed to the structural and chemical differences, and suggest that heat conductivity is determined mainly by the chain valence forces which, for all but two examples, are of the same general nature; that is, forces between carbon-to-carbon single and occasionally double bonds. If this view is correct, the thermal conductivity of a polydimethylsiloxane polymer



should differ appreciably from that of polyisobutylene:



This is seen to be the case for the two samples of Silastic listed in Table I, even though the argument is weakened somewhat by uncertainty as to exact polymer composition. It would be of interest to have further data for inorganic linear polymers, such as elastic sulfur, polyphosphonitrilic chloride, and silicon disulfide.

The sound velocity values listed in the last three columns of Table II show that Equation (9) yields results that are too large, by about an order of mag-

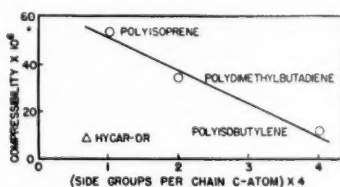


Fig. 3.—Effect of chemical structure on compressibility.



nitide, when compared with the values given in the next to the last column, which were computed from the mechanics formula,  $v$  (infinite) =  $(V_{sp}/\kappa)^{1/2}$ , for the velocity of a compression wave in an infinite medium. The value thus obtained for natural rubber,  $1.43 \times 10^3$  m. per sec., agrees fairly well with a measured value of  $1.6 \times 10^3$  m. per sec. recently reported<sup>16</sup> for the frequency region from 10 to 50 kilocycles. Exner's experimental value for natural rubber<sup>25</sup> given in the last column of Table II is only in apparent disagreement<sup>26</sup> with that value given by the mechanics formula. He carried out his measurement with a free bar of rubber, and it is known that a longitudinal wave in such a system has a velocity given by  $v$  (finite) =  $(V_{sp}/E)^{1/2}$ . Since the bulk modulus for rubbers is  $10^3$  to  $10^4$  times as great as Young's modulus,  $v$  (infinite) should be of the order of fifty times as great as  $v$  (finite)—in agreement with the tabulated results.

The inapplicability of Equation (9) to the rubberlike state cannot be attributed to the roughness of the model used in its derivation, in view of its successful description of liquid systems, and therefore serves to emphasize that rubbers are not liquid in the sense that their properties are derivable by laws known to apply to ordinary liquids. A recent theoretical treatment<sup>27</sup> of the transfer of momentum in amorphous bodies has found it necessary to invoke not only the shear viscosity, but also a volume viscosity that may arise from a relaxation mechanism of any kind connected with reversible shear deformations in such systems—at least five and more generally seven elastic and viscous constants being required to characterize the amorphous body. Orientation effects were concluded to play an essential role.

Finally, it is of interest to point out one further consequence of the specific heat theory, which pertains to cross-linking and branching. On the basis chiefly of chemical analysis, it has occasionally been proposed that as many as 10 or 20 per cent or more of polymer double bonds are consumed through the occurrence of cross-linking processes in certain butadiene polymers or copolymers. While such values have seemed inordinately high, on the grounds of other considerations, the point has been difficult to prove. According to theory, the specific heat of a netted polymer should vary as  $T^2$  at Debye temperatures, as shown in Equation (11). It can be inferred that branching, as this term is commonly understood, should give a temperature dependence somewhere in the region between  $T^1$  and  $T^2$ . There is no evidence for any but linear temperature dependence in the specific heat curves considered<sup>28</sup>, even though two of these are for butadiene derivatives. While it is not meant to suggest that these polymers are devoid of cross-linking or branching, it is considered that, if these effects are as large as is occasionally proposed, the influence on the course of the specific heat curve should be immediately apparent.

#### ACKNOWLEDGMENT

The author wishes to thank John A. Thomas for making most of the thermal measurements, A. H. Gleason for the synthesis of one of the polymers, and various members of the technical staff for compounding and preparing the test-specimens.

#### SUMMARY

In this paper experimentally determined values are reported for the thermal diffusivity ( $k$ ) of various rubberlike polymers. Corresponding values of the thermal conductivity ( $W$ ) can be computed from the well-known relationship,



$W = k\rho c_P$ , where  $\rho$  and  $c_P$  denote the density and specific heat at constant pressure of the composition. Measurements were made on (1) pure-gum stocks prepared with natural rubber, Butyl (GR-I), Perbunan-18, Perbunan-26, Perbunan-35, Buna-S (GR-S), polybutadiene, Neoprene-GN, polyisoprene, Silastic-160, and Silastic-180; (2) pure-gum stocks of the first five rubbers listed under (1) containing in addition 20 parts of a hydrocarbon softener (Bardol), based on 100 parts by weight of the polymer; and (3) the Bardol stocks containing in addition 54 parts of carbon black (Kosmobile-66). From measurements of the rate of change of temperature within a rubber sphere suddenly subjected to a change in its surface temperature, it was found possible to determine the dependence of  $k$  on temperature. A satisfactory definition of the "mean" temperature of a sphere under these conditions is described. In a discussion of the effect of chemical composition and structure on heat conduction, the bearing of hindered rotation, cross-linking and branching and interatomic bond strength on the results is pointed out. Values are derived for certain other properties of some of the polymers, including their characteristic Debye temperatures, specific heats at constant volume, flexibility of the main valence chains, compressibilities, and sound velocities.

## REFERENCES

- <sup>1</sup> For a bibliography see Memmler, "The Science of Rubber", translated by Dunbrook and Morris, Reinhold Publishing Corp., New York, 1934, p. 463.
- <sup>2</sup> Jacobi, *Kunststoffe* **32**, 10 (1942); "Resins, Rubbers, and Plastics", Interscience Publishers, Inc., New York, 1942.
- <sup>3</sup> Houwink, "Chemie und Technologie der Kunststoffe", Akad. Verlagsgesellschaft, Leipzig, 1942, Vol. 2, Tables 79 and 82.
- <sup>4</sup> Frumkin and Dubinker, *Kauchuk i Rezina* **1939**, p. 25; *RUBBER CHEM. TECH.* **13**, 361 (1940).
- <sup>5</sup> Müller and Houwink, "Chemie und Technologie der Kunststoffe", Akad. Verlagsgesellschaft, Leipzig, 1942, p. 226; Schäfer, *Fette u. Seifen* **49**, 585 (1942).
- <sup>6</sup> Byerly, "Fourier's Series and Spherical Harmonies", Ginn & Co., Boston, 1919, p. 116.
- <sup>7</sup> Williamson and Adams, *Phys. Rev.* **14**, 99 (1919).
- <sup>8</sup> Carslaw, "Conduction of Heat in Solids", Dover Publishing Co., New York, 2nd Ed., 1945, p. 14.
- <sup>9</sup> Byerly, "Fourier's Series and Spherical Harmonies", Ginn & Co., Boston, 1918, p. 122.
- <sup>10</sup> Hahn, *J. Applied Physics* **12**, 12 (1941).
- <sup>11</sup> Schallamach, *Nature* **145**, 67 (1940); *Proc. Phys. Soc. London* **53**, 214 (1941).
- <sup>12</sup> Müller, in Houwink, "Chemie und Technologie der Kunststoffe", Akad. Verlagsgesellschaft, Amsterdam, 1942, Vol. I, p. 226.
- <sup>13</sup> Meyer, "Natural and Synthetic High Polymers", Interscience Publishers, Inc., New York, 1942, p. 159.
- <sup>14</sup> Jeffreys, *Proc. Cambridge Phil. Soc.* **24**, 19 (1928); Bridgman, "Physics of High Pressure", Macmillan, New York, 1931, p. 317; Powell, Roseveare and Eyring, *Ind. Eng. Chem.* **33**, 430 (1941).
- <sup>15</sup> Bridgman, "Physics of High Pressure", Macmillan, New York, 1931.
- <sup>16</sup> Boyer and Spencer, in Mark and Whitby, "Advances in Colloid Science", Interscience Publishers, Inc., New York, 1946, p. 15.
- <sup>17</sup> Tarassov, *Compt. rend. acad. sci. U.R.S.S.* **46**, No. 1, 20 (1945); No. 3, 110 (1945).
- <sup>18</sup> Bekkedahl and Matheson, *J. Research Natl. Bur. Standards* **15**, 503 (1935).
- <sup>19</sup> Ferry and Parks, *J. Chem. Physics* **4**, 70 (1936).
- <sup>20</sup> Bekkedahl and Scott, *J. Research Natl. Bur. Standards* **29**, 87 (1942).
- <sup>21</sup> Buhemann and Simon, *Z. physik. Chem.* **A138**, 1 (1928).
- <sup>22</sup> Based on unpublished values for nitrile copolymers reported by several laboratories to the Office of Rubber Reserve. It is easily established that the final results are not sensitive to the probable error in this assumption.
- <sup>23</sup> See Flory, *J. Am. Chem. Soc.* **65**, 372 (1943); Evans and Polanyi, *Nature* **152**, 738 (1943); Brown and Barbaras, *J. Chem. Physics* **14**, 114 (1946).
- <sup>24</sup> Debye, P., unpublished results reported to the Office of Rubber Reserve.
- <sup>25</sup> Exner, Sitzber, *Akad. Wiss. Wien. Math. naturw. Klasse.* **69**, IIb, 102 (1874).
- <sup>26</sup> The author is indebted to L. A. Wood for this point.
- <sup>27</sup> Frenkel and Obrastsov, *J. Phys. U.S.S.R.* **2**, 131 (1940).
- <sup>28</sup> Ruhemann and Simon, *Z. physik. Chem.* **A138**, 1 (1928); Bekkedahl and Matheson, *J. Research Natl. Bur. Standards* **15**, 503 (1935); Ferry and Parks, *J. Chem. Physics* **4**, 70 (1936); Bekkedahl and Scott, *J. Research Natl. Bur. Standards* **29**, 87 (1942).

## LOW TEMPERATURE CHARACTERISTICS OF ELASTOMERS \*

S. D. GEHMAN, D. E. WOODFORD, AND C. S. WILKINSON, JR.

THE GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

Elastomers stiffen characteristically and suffer impairment of high elasticity at low temperatures. The practical limitations which this imposes on their respective fields of use has led to the development of many laboratory procedures for testing and evaluating low-temperature properties. A comparative discussion of the various published methods was undertaken by Liska<sup>1</sup> and Mullins<sup>2</sup>. A broad line of demarkation exists between two types of tests, brittleness and modulus tests, the theoretical relations for which have been elucidated by Boyer and Spencer<sup>3</sup>. It appears that the most generally applicable type of test is one which gives a measure of the stiffness over a range of temperatures low enough to include the transition region through which the long-chain molecules lose the ability to unkink or uncoil, so that the rubber becomes essentially an ordinary solid. Such modulus determinations have been made in a wide variety of ways, using either stretching, bending, or torsional deformations. The results have much in common, as they are obtained for relatively small slow deformations, which are more fundamental conditions than the type of deformation. This paper describes a simple and convenient torsion apparatus, which has been useful in securing this type of information, and illustrates the results obtained.

Mullins<sup>2</sup> discussed the difficulties in trying to evaluate low-temperature stiffening by a single value of the relative modulus. He suggested reporting the temperatures at which the relative modulus (ratio of modulus at low temperature to the modulus at 20° C) is two and ten. It seems preferable to report the entire modulus curve whenever possible, so that the rubber compounds can be compared in the temperature range of interest for each particular application. For some purposes it may be sufficient to report the relative modulus at a given temperature or at two temperatures bounding the range of interest.

Although a simple modulus or stiffness test is sufficient in a general way for many purposes and is a useful guide for compound and polymer development, in many cases it leaves large gaps in the information which is desirable for understanding low-temperature characteristics of rubber. If the use of the rubber involves circumstances which differ widely from the test conditions, such as rapid deformations, large deformations, or long exposure to low temperatures, which conditions are frequently encountered in service, the modulus and brittleness tests as ordinarily carried out are inadequate. To secure a correct perspective, it is then necessary to modify the test or to set up special test conditions to conform more closely to the service conditions. This work, in addition to giving results from the torsion modulus test, is concerned with some

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 39, No. 9, pages 1108-1115, September 1947. This paper was presented before the Division of Rubber Chemistry of The American Chemical Society at the 110th Meeting, Chicago, Illinois, September 10-13, 1946.

aspects of the low temperature behavior for rapid deformations, free retraction, and long exposures to low temperatures.

### LOW TEMPERATURE DEFORMATIONS

The kinetic theory of rubber elasticity explains the temperature dependence of the modulus of rubber on a thermodynamic basis which is generally regarded as being satisfactory. According to this theory the modulus decreases linearly with the absolute temperature. The experimental tests of the theory are usually carried out by relaxing the specimen to establish reversible conditions, stretching it at room temperature or higher, and then determining the modulus as the temperature is varied in steps<sup>4</sup>.

In contrast to these results, modulus measurements as ordinarily made, and which are discussed here, show increased stiffness at lower temperatures. The apparent contradiction is due to the different experimental procedures used. The theory applies to equilibrium conditions which are readily obtained by stretching the rubber and changing the temperature. In the usual type of measurement, on the other hand, the rubber is brought to the low temperature and then deformed. In another alternative the rubber may be deformed at the higher temperature and cooled so that it shows the normal Joule effect, but subsequent small deformations at low temperature indicate an increase in the modulus over that measured at the high temperature.

The theoretical explanation of these effects lies in the large influence of the time factor for low temperature deformations. The time for a rubber deformation to occur depends on molecular relaxation times which, in simple theory, depend exponentially on the temperature. For the usual type of measurement this effect more than counteracts the relatively small linear dependence on absolute temperature explained by the kinetic theory.

The situation can be better understood by reference to the mechanical model shown in Figure 1, which idealizes the rubber structure as a system of linear springs and dashpots. The mathematical solution for this model<sup>5</sup> gives the deformation due to a constant load at time  $t$  after load application as:

$$D(t) = \frac{P}{k_1 + k_2} \left[ 1 + \frac{k_2}{k_1} \left( 1 - e^{-t/\tau} \right) \right] \quad (1)$$

$$\tau = \eta \frac{k_1 + k_2}{k_1 k_2} \quad (2)$$

where  $k_1, k_2$  = spring stiffnesses

$\eta$  = viscosity of dashpot

The instantaneous deformation,  $t = 0$ , is given by the first term of Equation 1. The second term, which has a limiting value secured by making  $t = \infty$ , represents the contribution of high elasticity to the deformation. To extend the mechanical analogy to rubber, the relaxation time  $\tau$  is considered to be a function of temperature, according to the equation:

$$\tau = A e^{U/kT} \quad (3)$$

where  $U$  = energy of activation

$k$  = Boltzmann's constant<sup>6</sup>

Equations 1 and 3 show that longer periods of time are required to attain a given deformation at lower temperatures. For  $t = \infty$ , the deformation is  $P/k_1$ , and is independent of  $\tau$ . The kinetic theory deals with the relatively

small dependence of  $k_1$  on temperature—that is, equilibrium deformations obtained theoretically at  $t = \infty$ . The time factor, however, is of predominant importance for most low temperature measurements as carried out in practice because of the effect of the term containing  $\tau$ . The deformation at a finite experimental time,  $D(t)$ , is less than  $D(\infty)$ . This is interpreted as an increase in modulus.

This idealized model emphasizes the importance of time as a factor in low-temperature measurements for rubber, when the experimental time of measurement is of the same order of magnitude as the relaxation times. It is not to be expected that very good quantitative agreement would be secured with such a simple theory. It is known that an infinite distribution of relaxation times is probably involved in rubber deformations. Furthermore, the elastic and viscous elements may not be linear, and there may be structural effects. It does not seem obvious that the structure achieved in respect to molecular

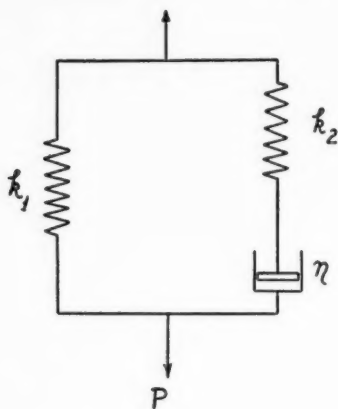


Fig. 1.—Mechanical model.

orientation, even after a long period of time in a specimen which is cooled and stretched, would be identical with that in the same specimen which was stretched and then cooled.

#### LOW TEMPERATURE TORSION TEST

Equipment for measuring torsional stiffness at low temperatures is shown in Figures 2 and 3. The test-pieces are small rubber strips died out from tensile test sheets. The dimensions are 1.625 inches long, 0.125 inch wide, and 0.079 inch thick. Five of these are fastened vertically in the Micarta grips of the cylindrical rack illustrated at the right in Figure 2. The top and bottom disks of the rack are also Micarta. The center post and the external freely turning studs are brass. The insulated chamber used is shown at the left of Figure 2. It is made of an inner aluminum tube 6.5 inches long and 3 inches in inside diameter, and an outer concentric tube of cadmium-plated steel, 4.5 inches in outside diameter. The space between the tubes is filled with insulating material held in place by Micarta rings pressed between the tubes at top and bottom. A Micarta disk having a 0.25-inch hole in the center is pressed in the bottom of the inner tube.

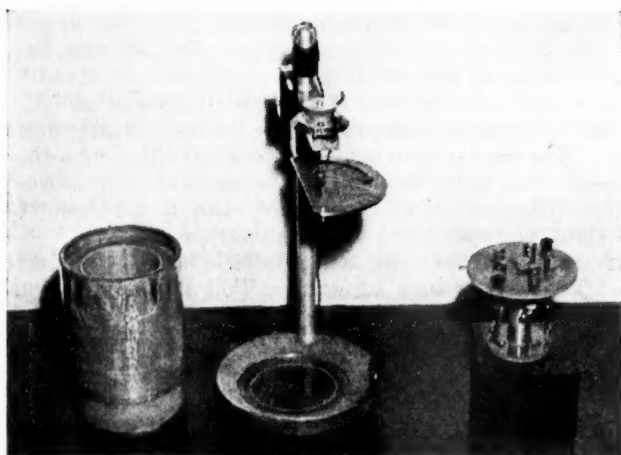


Fig. 2.—Parts of torsional stiffness tester.

The torsion head and stand are shown at the right in Figure 2. The base includes provision for introducing a stream of air in the bottom of the insulated chamber. The torsion wire is steel of 0.011-inch diameter and 2.38 inches long. A pointer is provided with a movable angular scale graduated in degrees for convenient, exact adjustment of the zero point.

Figure 3 shows the equipment as assembled for use. The stand is set in a shallow, insulated pan, which also contains a flat spiral of copper tubing for



Fig. 3.—Assembled torsional stiffness tester.

precooling the air introduced through the hole in the bottom of the insulated chamber. The air passes over acetone in the bottle as shown, to prevent frost formation. The pan is filled with lumps of dry ice moistened with acetone. Dry ice is also used in the bottom of the insulated chamber. Manual regulation of the air flow provides temperatures in the test chamber down to  $-90^{\circ}\text{C}$  if necessary. The temperature can be determined either by a thermometer or thermocouples. The latter have the advantage of faster response to temperature changes. The specimens are attached in turn to the torsion head by rotation of the chamber and use of a screw connection.

To measure the stiffness, the temperature is held at the desired value for 5 minutes. The scale is then adjusted so that the pointer is at zero. The torsion head is turned exactly  $180^{\circ}$ , and the pointer reading taken after 10 seconds. Readings are usually secured first at the lowest temperature and then at intervals of  $5^{\circ}$  or  $10^{\circ}\text{C}$  as the temperature is raised. An audible timer marks the 10-second waiting times.

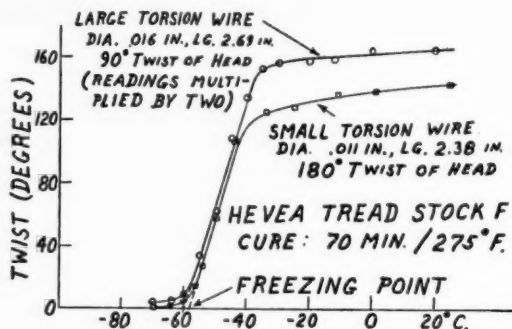


FIG. 4.—Typical plot of twist vs. temperature.

Figure 4 shows the type of curve obtained when the twist of the pointer is plotted against temperature. At the low temperature end the curve rises slowly until the transition region is reached, a sharp rise occurs, and then the curve flattens off again. If the transition portion of the curve is extrapolated backward to the temperature axis, a value of the temperature is indicated which is conveniently designated as the freezing temperature. The uncertainty in the extrapolation is usually about a degree; hence some subjectivity in the determination must be acknowledged. There may also be some dependence on the apparatus and testing procedure. Nevertheless, the curves in Figure 4 show that the freezing point is shifted only about  $2^{\circ}\text{C}$  when the constant of the torsion wire is changed by a factor of about four. Figure 5 shows a very small effect on the freezing point when the time for taking the twist readings after application of the torque is in the range 10 to 20 seconds. The stiffening point defined below is also insensitive in this range, since values for the 5-, 10-, and 20-second intervals are, respectively,  $-48.7^{\circ}$ ,  $-50.5^{\circ}$ , and  $-52^{\circ}\text{C}$ . At any rate, the freezing temperature serves the purpose of marking the start of the transition region for this torsion test. It does not seem to have any correlation with brittle points which have been reported for stocks similar to those tested here. Freezing points for Hevea and GR-S tread stocks are actually found to be in reverse order from reported brittle temperatures<sup>1</sup>, which give GR-S as having a lower brittle point than Hevea. This lack of correlation



is not surprising in view of the dependence of brittle temperature on the testing conditions<sup>7</sup> and the different character of the two determinations. Unless the service for a rubber compound actually includes the possibility of a low-temperature brittle failure, the freezing point appears to be a much more significant criterion for evaluating low temperature properties than does the brittle point.

The relative torsional modulus at any temperature is computed as the ratio of the modulus at the low temperature in question to the modulus at 25° C. The temperature for which this ratio is ten is called the stiffening point in this work. In many cases it is preferable to use the temperature corresponding to

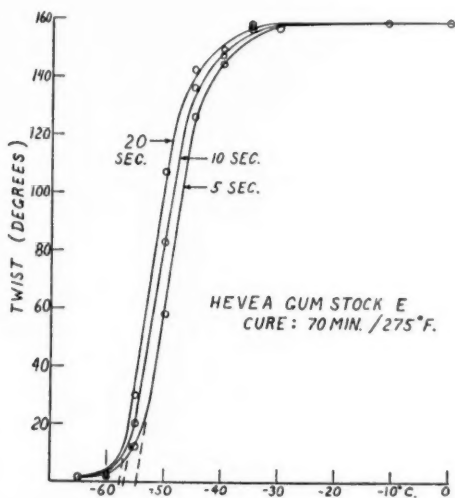


FIG. 5.—Effect of time interval on experimental curves.

a lower ratio than ten in order to characterize low temperature stiffening. The modulus is connected with the twist measurement by the relation:

$$\text{Modulus} \propto \frac{180^\circ - \text{twist}}{\text{twist}} \quad (4)$$

The numerator represents the torque applied to the test-piece. The torsion head is turned 180°, but the applied torque is reduced by the twist of the test-piece. The factor of proportionality in Equation 4 involves both the torsion constant of the wire and the geometry of the test-piece. Since only relative values of the modulus at different temperatures are of interest in this work, and since a geometrical factor calculated from the theory of elasticity for small deformations would be of doubtful applicability, these factors may be omitted. Values of the twist at various temperatures are taken from twist-temperature curves such as those illustrated in Figure 4. Corresponding values of the fraction  $(180^\circ - \text{twist}/\text{twist})$  are read from a table. The relative modulus can then be readily computed and plotted as a function of temperature. The principal compounds used are given in Table I.

TABLE I  
COMPUTED FORMULAS

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
GR-S	100.0	100.0	100.0	100.0	..	..	..	..	..	..	..	..	50.0	100.0
Smoked sheet	..	..	..	..	100.0	100.0	100.0	..	..	..	..	100	50.0	..
Neoprene-GN	..	..	..	..	..	..	..	..	100.0	..	..	..	50.0	..
Butyl	..	..	..	..	..	..	..	100.0	..	..	..	..	..	..
Chemigum N-3*	..	..	..	..	..	..	..	..	..	100.0	..	..	..	..
Chemigum N-4†	..	..	..	..	..	..	..	..	..	..	100.0	..	..	..
Sulfur	2.0	2.0	2.0	2.0	3.0	3.0	2.75	2.0	..	1.6	1.6	2.5	2.5	2.5
Zinc oxide	5.0	5.0	5.0	5.0	3.0	3.0	5.0	3.0	5.0	5.0	5.0	5.0	5.0	5.0
Softener	3.0	3.0	3.0	3.0	4.0	4.0	3.0	3.0	3.0	5.0	5.0	6.0	6.0	6.0
Phenyl-naphthyl-amine	..	..	..	..	1.0	..	..	..	1.0	..	..	..	..	..
Magnesia	..	..	..	..	..	..	..	..	4.0	..	..	..	..	..
Santocure	1.5	1.5	1.5	1.5	1.0	0.5	1.35	0.5	..	1.5	1.5	1.0	1.0	1.0
Captax	..	..	..	..	..	..	..	1.0	..	..	..	..	..	..
Tuads	2.0	2.0	2.0	2.0	4.0	1.0	3.0	3.0	3.5	0.5	0.5	1.0	1.0	1.0
Stearic acid	50.0	40.0	30.0	..	..	45.0	50.3	45.0	45.0	50.0	50.0	50.0	50.0	50.0
E.P.C. Carbon black	..	..	..	..	..	..	..	..	..	..	..	..	..	..

\* Copolymer of butadiene-acrylonitrile, 60/40.

† Copolymer of butadiene-acrylonitrile, 70/30.

## RESULTS OF MODULUS TESTS

Figures 6 to 14 exhibit the type of information which may be secured with the torsion modulus test described. Since the relative modulus curves plotted

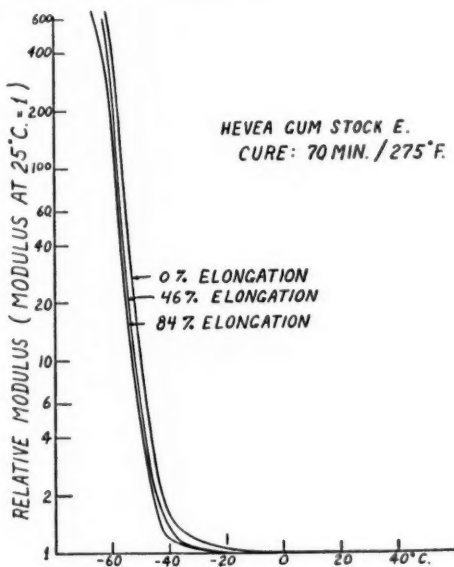


FIG. 6.—Effect of elongation on relative modulus.

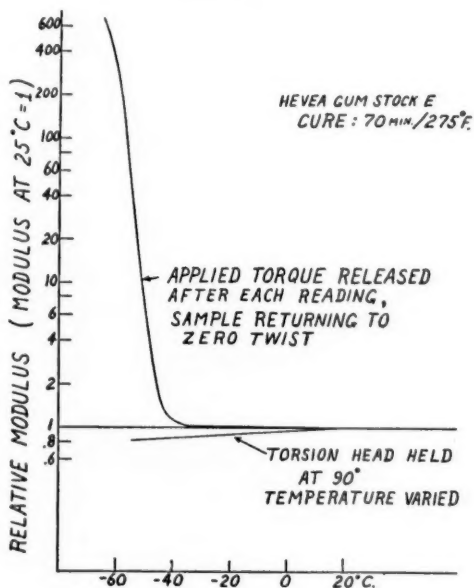


FIG. 7.—Experimental test of magnitude of modulus changes.

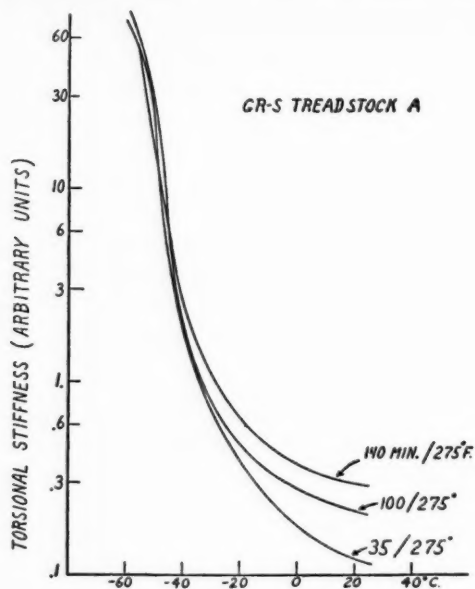


FIG. 8.—Effect of cure on stiffness.

in the figures are derived from smooth experimental twist curves such as those in Figure 4, which show little scattering of the points from the curves, there would be no object in entering points on the relative modulus curves.

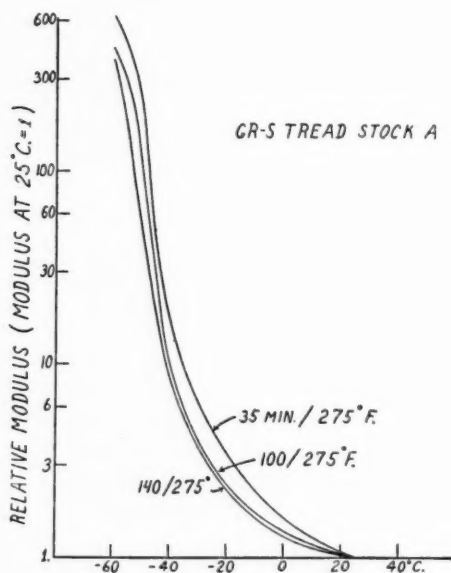


FIG. 9.—Effect of cure on relative cold hardening.

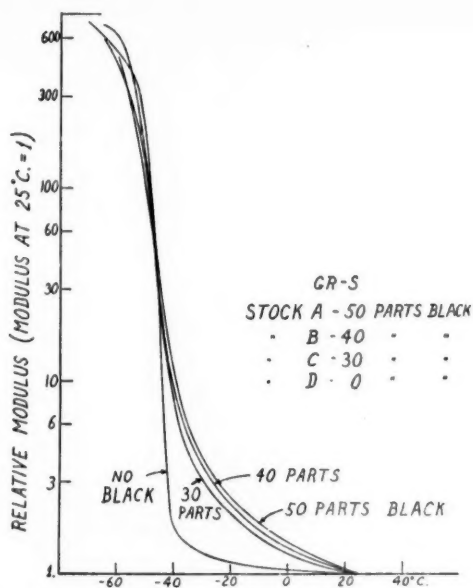


FIG. 10.—Effect of carbon black on relative cold hardening.

Figure 6 illustrates the small effect of superposed elongations on the results. Any accidental variation in the tension of the test-piece when installed for regular testing purposes is negligible.

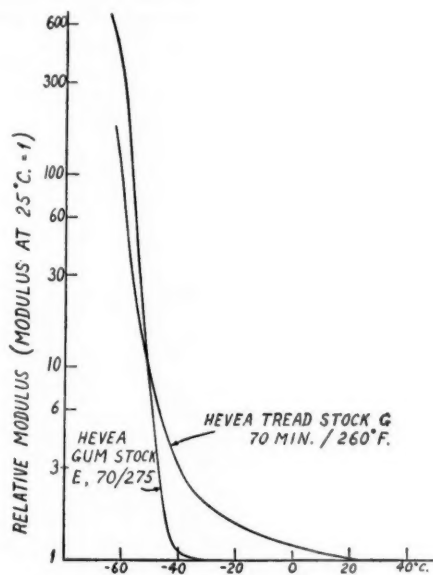


FIG. 11.—Cold hardening of natural rubber.

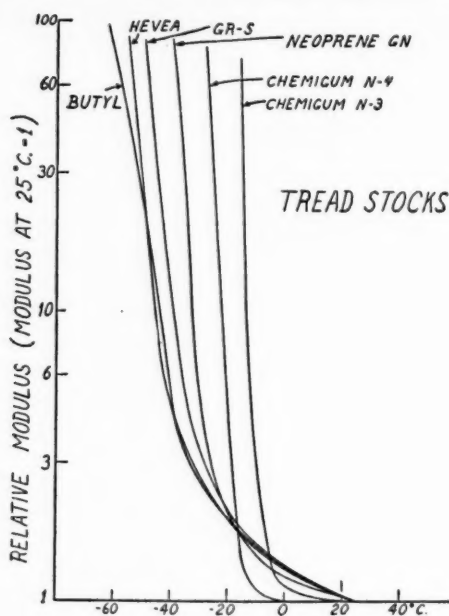


FIG. 12.—Cold hardening of various elastomers.

Figure 7 illustrates an experimental verification of the theoretical ideas previously discussed. When the torque is applied to the test-piece and the temperature is dropped, a small decrease in the apparent modulus is observed. When, on the other hand, the torque is applied after the sample is cooled, a large increase in stiffness is observed at lower temperatures.

Figure 8 is a plot of torsional stiffness against temperature for a series of cures of GR-S tread stock A. The curves show a rather small spread, considering the range of cures involved; nevertheless, the differences in stiffness at room temperature persist in a systematic way at moderately low temperatures. When, on the other hand, relative modulus is plotted against temperature

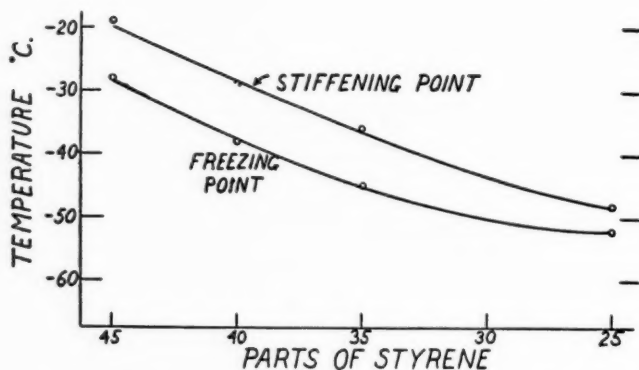


FIG. 13.—Effect of styrene content of on stiffening and freezing points GR-S.



(Figure 9), initial differences in stiffness are discounted, and the curves lie in the reverse order from those in Figure 8. The advantage of tight cures for resistance to the effect of low temperatures is thereby demonstrated. Cold hardening is usually considered to be due to increased secondary valence forces. Intermolecular distances decrease and molecular motions are hindered at low temperatures. Vulcanization, the forming of primary valence cross-linkages, does not usually affect the cold hardening process very greatly in a conventional range of technical cures.

Figures 10 and 11 are included to show the effect of carbon black loadings on the relative modulus at low temperatures. Carbon black increases the relative stiffening appreciably for the most important part of the temperature range and decreases the abruptness of the low temperature transition. These effects are no doubt connected with hindered molecular rotations and segmental

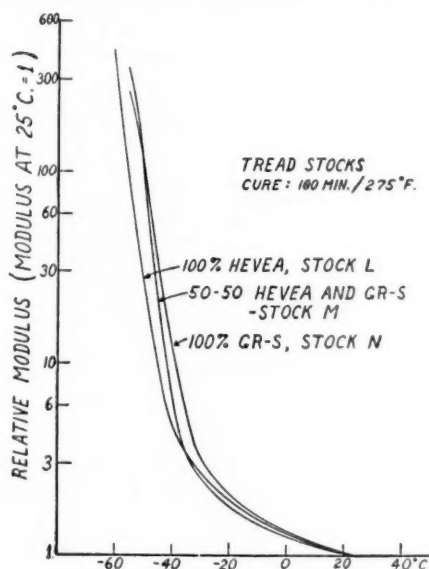


Fig. 14.—Cold hardening of a mixture of GR-S and Hevea.

movements due to the molecular anchorages at the carbon black particles. The proportional increase in stiffness becomes larger for each molecular segment immobilized as the number of mobile segments is reduced, in the same way that each successive increment of carbon black loading becomes increasingly effective in raising the modulus at room temperature.

Since cold hardening is dominated by secondary valence forces and the hindrance of segmental molecular motions, the chemical composition and chain form of the long-chain molecules are of paramount importance. These have much more influence than other features of the polymer structure, such as molecular weight and the primary valence network structure. This is brought out by the curves of Figure 12, which illustrate the wide range of cold hardening characteristics for a number of technically important elastomers. The Hevea and Butyl curves in Figure 12 are for compounds F and H, respectively. Liska<sup>1</sup> showed somewhat more spread between Hevea and Butyl. This may

be due, at least in part, to the different compounding used. Suitable compounding can get the best cold resistance and balance in physical properties from each type of rubber, but the selection of the best elastomer to start with for a particular low temperature application is very important. In general, when polar molecular groups are present, they tend to increase intermolecular forces. This leads to inferior low temperature properties. Side groups such as occur in the styrene molecules of GR-S can also be effective in hindering the molecular motions requisite for the best low temperature properties of a hydrocarbon polymer. Consequently, the low-temperature characteristics of GR-S are not so good as for polybutadiene or Hevea.

Figure 13 gives curves showing the rise in freezing and stiffening points caused by increased proportions of styrene in butadiene-styrene copolymers. The tread stocks for these data were formulated with 45 parts E. P. C. black and 1.6 parts of sulfur. Captax-diphenylguanidine acceleration was used. The proportion of styrene plotted is the charging ratio. Figure 14 compares the cold hardening of a 50-50 mixture of Hevea and GR-S with that of Hevea and GR-S controls.

#### LONG EXPOSURE TO LOW TEMPERATURES

It has been previously reported<sup>8</sup> that vulcanized compounds of Hevea and Neoprene crystallize and increase in stiffness on long exposures to low temperatures. We were particularly interested in determining whether this effect is a contributing factor to the low-temperature performance of Butyl rubber. Test pieces of Hevea, Butyl, Neoprene, and GR-S tread stocks were therefore mounted in the torsional stiffness tester. This was placed in a cold room at  $-30^{\circ}\text{C}$ . Observations of the torsional stiffness were made periodically. The results are shown by the curves in Figure 15. Neoprene, Hevea, and Butyl

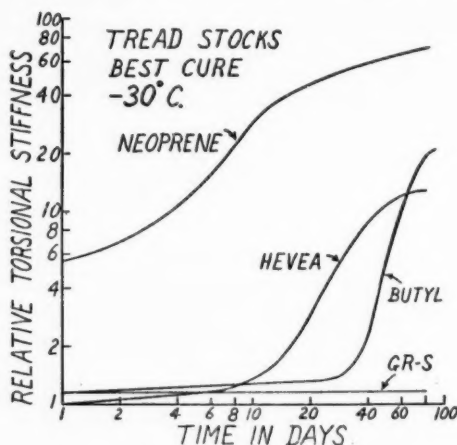


Fig. 15.—Torsional stiffness for long exposures.

showed large increases in stiffness after varying induction periods, which were surprisingly long. GR-S did not do this. Since Neoprene, Hevea, and Butyl crystallize on stretching and GR-S does not, crystallization would be the obvious explanation for the observations, despite the fact that crystalline x-ray

patterns have never been reported for well vulcanized compounds of unstretched Hevea and Neoprene, or for unstretched Butyl rubber, either vulcanized or unvulcanized. It seemed worth while to secure x-ray diffraction patterns when the test was discontinued. The procedure was as follows:

A piece of 0.5-inch-diameter copper tubing was soldered through the bottom of a quart paint can. Holes were drilled through the tube to serve as windows for the x-ray beam. In the cold room the specimen was mounted in the copper tube between the windows, which were then covered with a very thin film of vulcanized rubber. The can was filled with dry ice moistened with acetone, and the lid put on. The vapors from the dry ice flowed down over the sample and kept it frozen during the x-ray exposure. The diffraction pattern secured for the Hevea and Butyl stocks are reproduced in Figure 16.

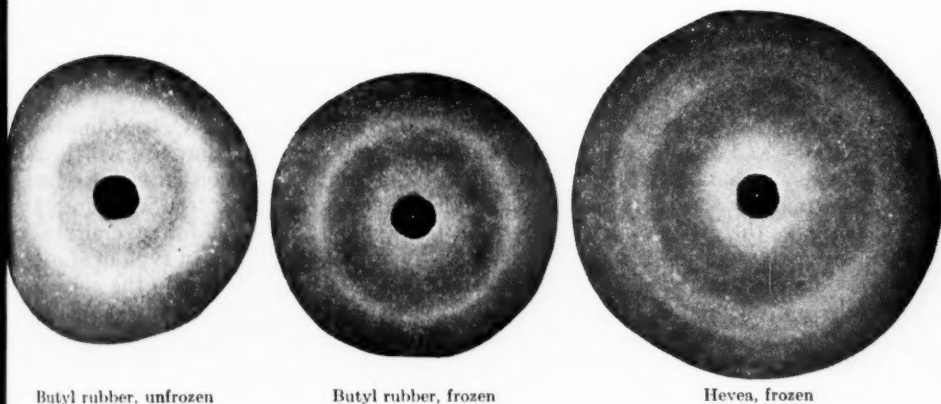


FIG. 16.—X-ray diffraction patterns.

The Hevea sample was crystallized. The pronounced sharpening of the ring in the Butyl pattern is also considered to be definite evidence of crystallization.

#### RAPID DEFORMATIONS AT LOW TEMPERATURES

The information secured from a modulus test such as has been described may be inadequate for accurate anticipation of the relative cold hardening for rapid deformations. The theoretical background for this has already been discussed. When the molecular relaxation times reach the same order of magnitude as the frequency, a considerable dependence of stiffness on frequency is to be expected. As the temperature is lowered, the molecular relaxation times increase, and the stiffness for rapid deformations increases more rapidly than it does for slow deformations. Figure 17 shows the effect of a moderate reduction in temperature on the resonance response of a GR-S tread stock at 3600 cycles per minute. The data were secured with the Goodyear resonance vibrator<sup>9</sup>. The resonance curve becomes broad and flat even at 0° C, and the peak shifts its position because of the increased stiffness.

At lower temperatures the elastomer structure is no longer able to respond to rapidly applied forces by the unkinking and uncoiling of the long chain molecules. Under such circumstances, for all intents and purposes, it ceases to have the property of high elasticity. The stiffness, as determined from

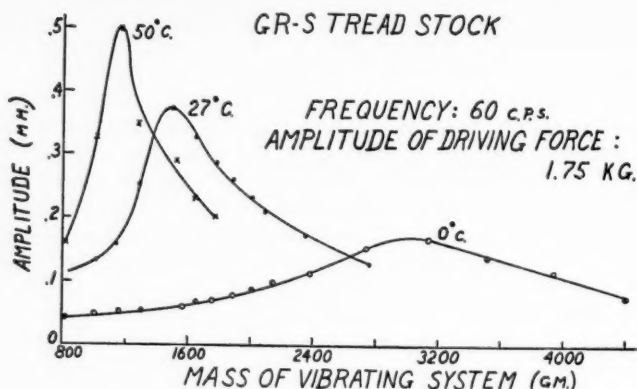


Fig. 17.—Effect of temperature on resonance curves.

resonance curves as broad as the one shown in Figure 17 at 0° C, is of limited accuracy and significance, but values are plotted for what they are worth in Figures 18 and 19. Figure 18 compares the relative changes in stiffness as measured by the vibration test and the torsional modulus test. Figure 19 compares the effect of temperature on the dynamic modulus for several synthetic polymers and for Hevea. It is possible that the ordinary type of static modulus test might be generally satisfactory for rating polymers in the correct order for low temperature dynamic service, but any specific value of the modulus thus determined would depart rather widely from the dynamic values, even at moderately low temperatures.

One of the most sensitive measures for the effect of low temperatures on elasticity is the speed of free retraction when the sample is released after stretching. The velocity of retraction depends on both the modulus and internal friction. The apparent modulus is higher at lower temperatures, as has been explained, but the dependence of this increased modulus on increased internal friction is indicated by reduced velocities of retraction. Equipment for measuring the speed of free retraction has been already described in detail<sup>10</sup>. The

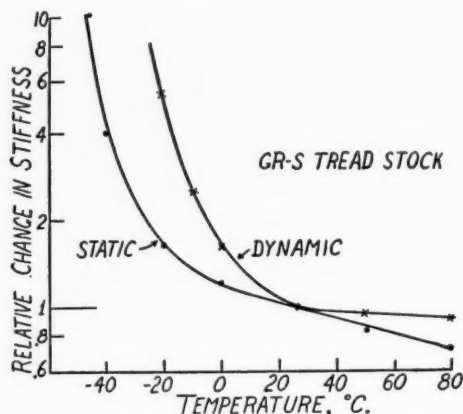


Fig. 18.—Relative effect of temperature on dynamic and static stiffness.

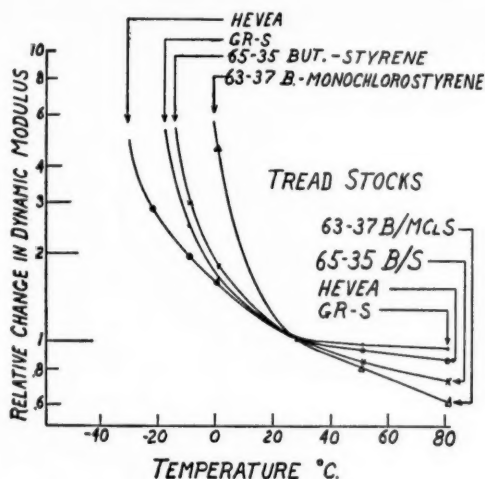


FIG. 19.—Relative effect of temperature on dynamic modulus.

apparatus was provided with a low temperature jacket (Figure 20). The jacket consists of two longitudinal compartments, one containing a pan of dry ice, the other the test piece. Air is circulated over the dry ice and through the sample compartment by means of a small variable-speed fan. The temperature is controlled by manual adjustment of the fan speed. Suitable baffles to control the air flow in the sample compartment ensure constancy of temperature along the stretched sample to about  $\pm 2^\circ \text{F}$ .

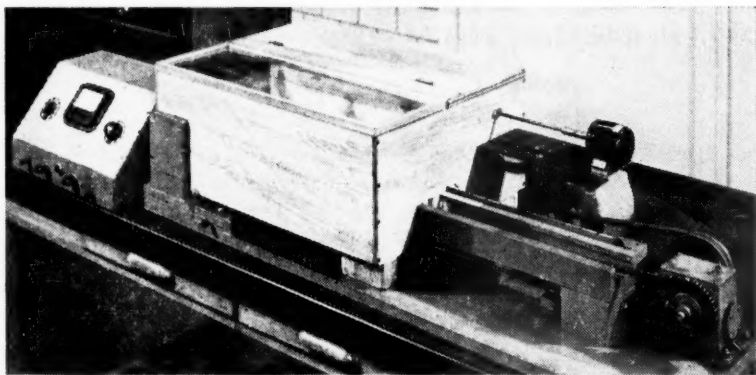


FIG. 20.—Speed of retraction apparatus.

Figures 21 and 22 compare speed of retraction results for Butyl, Hevea, and GR-S tread stocks at room temperature,  $25^\circ \text{C}$ , and  $-1^\circ \text{C}$ . The test pieces were cooled, stretched, and held for 1 minute before release. Inspection of the curves shows a startling deficiency in elasticity for Butyl rubber at the lower temperature as compared to Hevea and GR-S. This would never be suspected from modulus measurements such as were plotted in Figure 12.

There Butyl seems to be about on a par with the other two in the persistence of its rubberlike character at low temperatures. The speed of retraction test is more critical and hence should be of considerable value to supplement the more conventional modulus data in the development of better compounds and polymers for low temperature service.

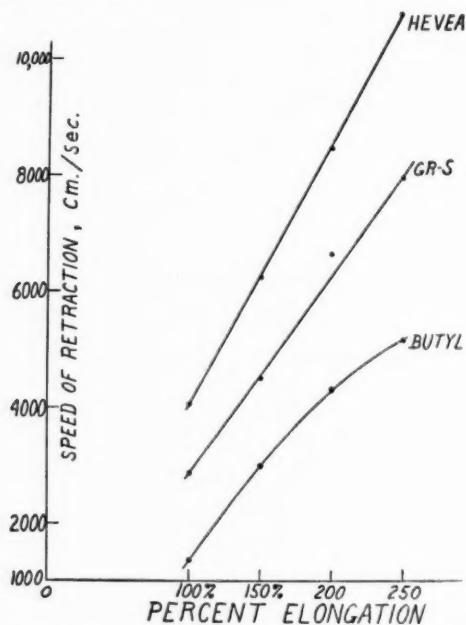


FIG. 21.—Comparison of retraction velocities at room temperature (25° C).

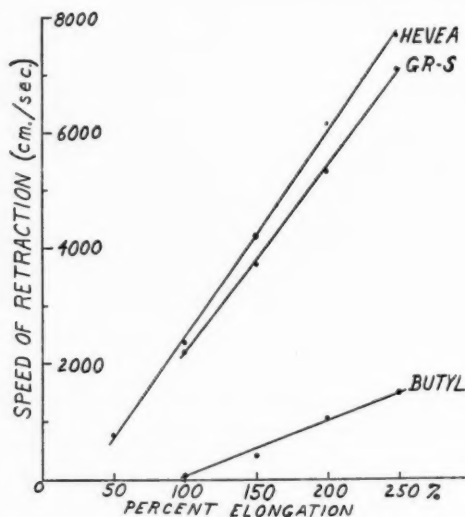


FIG. 22.—Comparison of retraction velocities at reduced temperature (-1° C).



## SUMMARY

The low temperature stiffening of elastomers frequently limits their usefulness. A new laboratory test for measuring their stiffness at low temperatures is described. Strips of the stocks to be tested are mounted around a cylindrical rack in a vertical, cylindrical insulated chamber. The temperature in the chamber is controlled by cooling the base externally with dry ice and by a moderate regulated flow of precooled air through dry ice in the bottom of the chamber. This system gives stable temperatures which are easily controlled. The chamber can be rotated to attach the samples in succession, by means of projecting top grips, to a suitably mounted torsion wire. The stiffness is measured by the angle of twist of the sample when the torsion head is rotated 180°. The relative modulus for any temperature is calculated as the ratio of the modulus at this temperature to that at 25° C. Plots of angle of twist against temperature show a rather sharp break at the low temperature end of the curve. This determines a somewhat subjective "freezing point". Curves are given to illustrate the wide variety of low temperature stiffening characteristics for elastomers. In unplasticized stocks the chemical composition of the monomers is the dominating factor for these properties for various synthetic rubbers. The stiffness of elastomers which are capable of crystallization on stretching, such as Hevea, Neoprene, and Butyl rubber, depends not only on temperature but also on time of exposure. To study these effects, the foregoing apparatus was used in a cold room. A rather long induction period occurs, during which the stiffness is essentially constant. It then increases and eventually reaches a larger constant value. Several months may be required to complete these changes. x-Ray examination of Hevea and Butyl proved that the increased stiffness on long exposure is due to crystallization. No change was observed in the stiffness of GR-S in the period of 2.5 months at -30° C. Reduction in the speed of retraction is a critical measure of the deterioration of high elasticity at low temperatures. It gives a wide differentiation at moderately low temperatures between Butyl rubber and Hevea or GR-S, whereas a slow modulus test does not.

## ACKNOWLEDGMENT

The authors wish to express their thanks to The Goodyear Tire & Rubber Company and L. B. Sebrell for permission to publish this work, to H. J. Osterhof for his encouragement in the work, and to G. H. Gates and J. H. Fielding for furnishing the compounds used. This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the government's synthetic rubber program.

## REFERENCES

- <sup>1</sup> Liska, *Ind. Eng. Chem.* **36**, 40 (1944).
- <sup>2</sup> Mullins, *Trans. Inst. Rubber Ind.* **21**, 247 (1945).
- <sup>3</sup> Boyer and Spencer, "Advances in Colloid Science", Interscience Publishers, Inc., New York, 1946, Vol. 2, p. 1.
- <sup>4</sup> Wood and Roth, *J. Applied Physics* **15**, 740 (1944).
- <sup>5</sup> Leaderman, "Elastic and Creep Properties of Filamentous Materials", Textile Foundation, Washington, 1943, p. 56; Bilmes, *J. Sci. Instruments* **22**, 16 (1945).
- <sup>6</sup> Aleksandrov and Lazurkin, *J. Tech. Physics (USSR)* **9**, 1249 (1939); *RUBBER CHEM. TECH.* **13**, 886 (1940).
- <sup>7</sup> Kemp, Malm, and Winspear, *Ind. Eng. Chem.* **35**, 488 (1943).
- <sup>8</sup> Conant and Liska, *J. Applied Physics* **15**, 767 (1944); Forman, *Ind. Eng. Chem.* **36**, 738 (1944); Liska, *Ind. Eng. Chem.* **36**, 40 (1944).
- <sup>9</sup> Gehman, Woodford and Stambaugh, *Ind. Eng. Chem.* **33**, 1032 (1941).
- <sup>10</sup> Stambaugh, Rohner, and Gehman, *J. Applied Physics* **15**, 740 (1944).

## VARIATION IN THE SPECIFIC HEAT OF RUBBER AS A FUNCTION OF ELONGATION \*

ANDRÉ MAYOR

LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF NEUCHÂTEL, NEUCHÂTEL, SWITZERLAND

The theory developed by Vogt<sup>1</sup> requires that the specific heat of stretched rubber be independent of the elongation, provided that the stress at constant elongation varies linearly with the temperature. Hamill, Mrowca and Anthony<sup>2</sup> have shown that the theory of Vogt is no longer applicable when a second phase is formed as a result of stretching.

According to measurements by Ornstein, Wouda and Eymers<sup>3</sup>, the specific heat of vulcanized rubber varies considerably with the elongation, passing through a minimum (only 65 per cent of the initial value) at an elongation of the order of 100 per cent. These latter measurements were concerned with the mean specific heats between 80° C and room temperature. With an apparatus with which it was possible to estimate the true specific heat at room temperature, Boissonnas<sup>4</sup> repeated these measurements and obtained results very different from those of Ornstein, Wouda and Eymers. The specific heat of a sample of unvulcanized rubber did not vary more than 3 per cent between rest and 200 per cent elongation, whereas the specific heat of a sample of vulcanized rubber varied more than 10 per cent between rest and 400 per cent elongation.

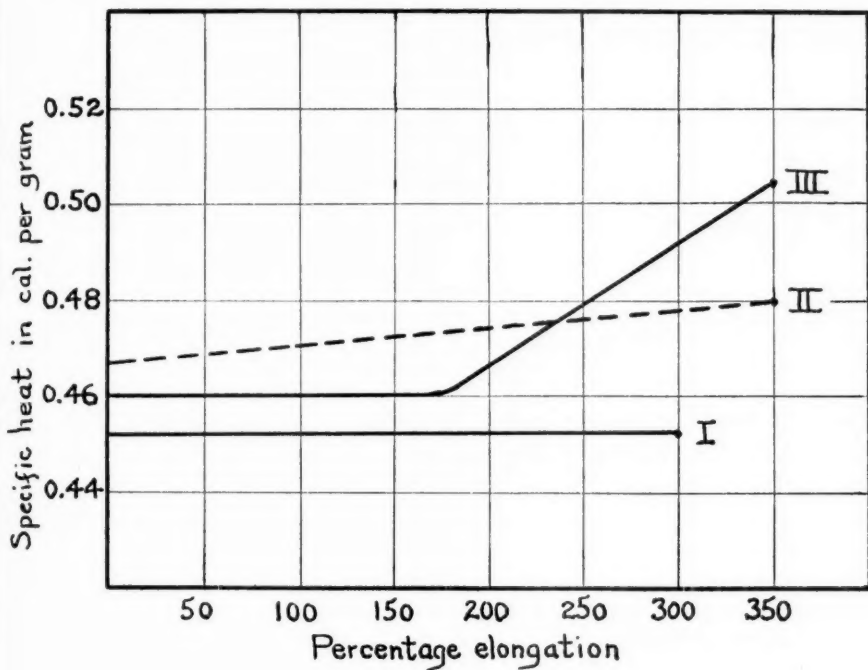
It seemed to the present author of interest to repeat these last measurements under conditions of greater precision. The calorimeter employed, which was developed from that used by Boissonnas<sup>4</sup>, was of the Nernst-Eucken type. On a Dellite roll<sup>5</sup> (15 mm. diameter, 0.4 mm. thick, and 90 mm. long) were wound a platinum wire as a thermometer and a constantin wire for heating. A rubber cord (square cross-section 3-4 sq. mm., and about 2 m. long) was coiled on this support at the desired elongation, and the whole system was suspended in a container within which a vacuum was maintained. The whole assembly was placed in a thermostat. The energy supplied by the heating current raised the temperature of the rubber about 1° C.

Because of the large thermal losses resulting from the low heat capacity and great surface of the apparatus, the temperature-time curve deviated too much from a straight line during cooling (the final phase of the measuring) to make it possible to calculate the correction by means of the classic formula of Regnault and Pfaundler. A very simple method was used, which is applicable to any calorimetric measurement in which the temperature change is definitely exponential. A graph was constructed on semilogarithmic paper on which the abscissa was a linear scale representing time and the ordinate was a logarithmic scale representing temperature. The angular coefficient of the straight line obtained in this way gives the coefficient of the Newton formula. The reproducibility of the measurements is as good as  $\pm 0.2$  per cent, although the correction for the thermal loss is of the order of 8 per cent.

Measurements of a sample of unvulcanized rubber (a cord cut from sheet) carried out at 25° did not show any change in specific heat when the rubber was

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY, from *Experientia*, Vol. 3, No. 1, pages 26-27 January 15, 1947.

stretched from 0 to 300 per cent (see curve I in the Figure). Samples of vulcanized rubber, when elongated from 0 to 350 per cent, behaved in two different ways. With two of the samples, whose stresses at constant elongation increased linearly with rise in temperature, the specific heats increased slightly with increase in elongation, *i.e.*, a linear increase of approximately 0.002 calorie per gram per 100 per cent elongation (see curve II in the Figure). With three more samples, the specific heats did not change at low elongations, then passed through a transition point, which at 25° C was at approximately 200 per cent elongation, above which point the specific heat increased relatively rapidly, *viz.*, 0.015–0.020 calorie per gram per 100 per cent elongation; in other words, ten times more rapidly than for the other two samples (see curve III



of the Figure). At a lower temperature, *i.e.*, 13° C, this transition point was at very small elongations. For the last three samples described above, the change in stress at constant elongation as a function of temperature was no longer linear and reversible above the elongation corresponding to the transition point found in the measurements of the specific heats.

It may be assumed, on the basis of the work of Meyer and Ferri<sup>6</sup>, that the transition point represents the sudden formation of a crystalline phase, the growth of which increases with increase in elongation. This would seem to be supported by the fact that, at the temperature at which the measurements in the present work were made, Bekkedahl and Matheson<sup>7</sup> proved that the specific heat of crystallized rubber is greater than that of amorphous rubber. This crystallization has still to be confirmed by *x*-ray examination.

Measurements made with a Neoprene thread<sup>8</sup> again showed a transition

point, the displacement of which with lowering of the temperature was greater than the displacement found with natural rubber under the same conditions.

### SUMMARY

The changes in specific heat of several samples of rubber when stretched were measured. Unvulcanized rubber showed no change in specific heat when it was stretched up to 300 per cent. The specific heat of vulcanized rubber increased very slightly and in proportion to the elongation. With some of the samples, a bend in the curve appeared at about 200 per cent elongation at room temperature, in which case the linear increase in specific heat was about ten times at higher elongations. Supposedly this sudden increase in specific heat is related to the heat of crystallization.

### REFERENCES

- <sup>1</sup> Vogt, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., New York, 1937, p. 375.
- <sup>2</sup> Hamill, Mrowca and Anthony, *Ind. Eng. Chem.* **38**, 106 (1946); *RUBBER CHEM. TECH.* **19**, 622 (1946).
- <sup>3</sup> Ornstein, Wouda and Eymers, *Proc. Acad. Sci. Amsterdam* **33**, 273 (1930); *RUBBER CHEM. TECH.* **3**, 403 (1930).
- <sup>4</sup> Boissonnas, *Ind. Eng. Chem.* **31**, 761 (1939); *RUBBER CHEM. TECH.* **12**, 794 (1939).
- <sup>5</sup> Bakelite paper, manufactured by the Fabrique Suisse d'Isolants, Bretonbac, Switzerland.
- <sup>6</sup> Meyer and Ferri, *Helv. Chim. Acta* **18**, 583 (1935); *RUBBER CHEM. TECH.* **8**, 319 (1935).
- <sup>7</sup> Bekkedahl and Matheson, *J. Research Natl. Bur. Standards* **15**, 503 (1935); *RUBBER CHEM. TECH.* **9**, 264 (1936).
- <sup>8</sup> This Neoprene thread was Lyntron, manufactured by the United States Rubber Co.

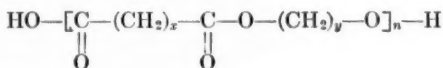
## RUBBERLIKE PRODUCTS FROM LINEAR POLYESTERS \*

B. S. BIGGS, R. H. ERICKSON, AND C. S. FULLER

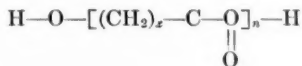
BELL TELEPHONE LABORATORIES, MURRAY HILL, N. J.

The polymers which result from the condensation of dibasic acids with propylene glycol are viscous gums which can be vulcanized to rubberlike products. In the unpigmented condition these rubbers are quite weak, but when reinforced with suitable pigments their strength and elongation compare favorably with other synthetic rubbers. Because polyesters of known structure and molecular weight can be easily synthesized, these polymers are useful for the study of the relations between structure and properties in rubberlike materials in general. Factors affecting tensile strength, oil resistance, brittle temperature, and stability are discussed.

The development of rubberlike products from linear polyesters was announced in a short news article more than three years ago<sup>1</sup>, but a detailed description of their preparation and physical properties has not been published. The object of this paper is to review these properties. However, the paper is written not so much from the viewpoint of offering a synthetic rubber for practical use as from that of applying linear polyesters to the study of the relations between structure and properties of rubberlike substances in general. As has been pointed out in other articles<sup>2</sup>, the linear polyesters are well suited to serve as models in such a study, since molecules of definitely known constitution and molecular-weight distribution can be synthesized by relatively simple methods. Furthermore, the chemical structure of the polyester chain molecules can be varied in a definite and controlled manner by the choice of suitable glycol and dibasic acid or hydroxy acid reactants. The structure of the chains in the case of the former, assuming equal molar proportions, may be represented by the general formula:



where  $x$  and  $y$  are integers greater than 1 and  $n$  is usually above 50 on the average. A polymer from a hydroxy acid has a simpler structure:



In all cases only linear chains are present, provided strictly bifunctional starting ingredients have been used. Thus many of the ambiguities of structure which complicate diene polymers (such as *cis* and *trans* orientations, 1,2 and 1,4 addition, etc.) are avoided. Finally, because of the known molecular-weight distribution, the number average molecular weight, on which the physical properties mainly depend, can be readily determined from viscosity measurements<sup>3</sup>.

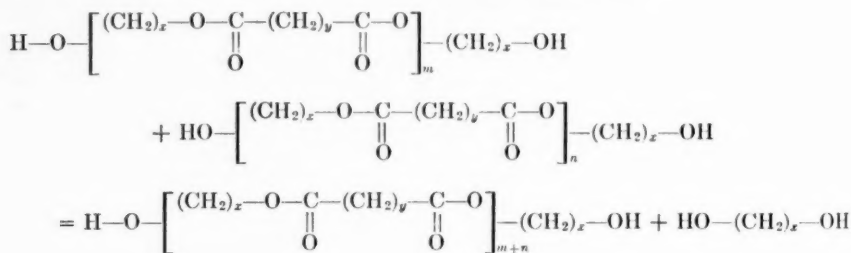
\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 39, No. 9, pages 1090-1097, September 1947.

## PREPARATION OF POLYESTERS

Polyesters are prepared by condensation of glycols with dibasic acids, or by self-condensation of hydroxy acids. A more diverse series of compounds is possible from the glycol dibasic acid polymers, since the availability of appropriate hydroxy acids is extremely limited; therefore the remainder of this discussion is confined to the former type of reaction.

The general method of preparation consists of two steps. In the first, a mixture of the dibasic acid and an excess of glycol containing a trace of catalyst—for example, 0.01 per cent zinc chloride—is esterified by being heated at a temperature from 200° to 260° C, depending on the nature of the reactants. Succinic esters darken badly, and adipic esters decompose with formation of cyclopentanone at temperatures above 220° C, whereas sebacic acid can be used satisfactorily at as high as 260° C or higher. Similarly some glycols decompose at high temperatures. The esterification is carried out under a reflux column heated to such a temperature that water cannot condense and glycol cannot escape. The reaction ingredients are stirred continuously and are kept under an inert atmosphere, preferably of hydrogen. In laboratory runs both results can be accomplished by passage of a rapid stream of dry, oxygen-free hydrogen through the mixture. Esterification may take one-half to several hours, depending on the size of the batch and the efficiency of the apparatus, and may be considered complete for practical purposes when a cold surface held against the outlet tube shows no condensation of moisture.

At this point the product consists of low polymer, with glycol residues on each end of every chain. The next step consists of a vacuum treatment, during which the chain length is built up by ester interchange<sup>4</sup> between the small units of polymer with resultant elimination of glycol, which distills away. This reaction is illustrated by the following general equation:



For this step the reflux column is replaced by a very short distillation head, which is wired for heat and is kept at a temperature such that no condensate forms in it. The pressure is reduced slowly to less than 5 mm., the flow of hydrogen being adjusted accordingly, and glycol is distilled off as fast as it is formed. Small amounts of cyclic ester also are found in the distillate. Ester interchange is quite rapid at first while the mixture is limpid, but as the viscosity increases, because of increased molecular weight, the rate of interchange falls off, and a point is finally reached at which the rate is so slow that continuation of the reaction becomes unprofitable. For small laboratory batches (about 50 grams, Figure 1) the time required under favorable circumstances—that is, with reactants which can be run at 250° C—is about 3 hours. At lower temperature or with larger batches a longer time is required. Efficient stirring is of the greatest importance, particularly after the product becomes



viscous, and a powerful and efficient mechanical agitator saves many hours of preparation time on large batches.

At the end of a run the polymer is poured or scraped while hot into large flat pans which have been dusted with talc or whiting.

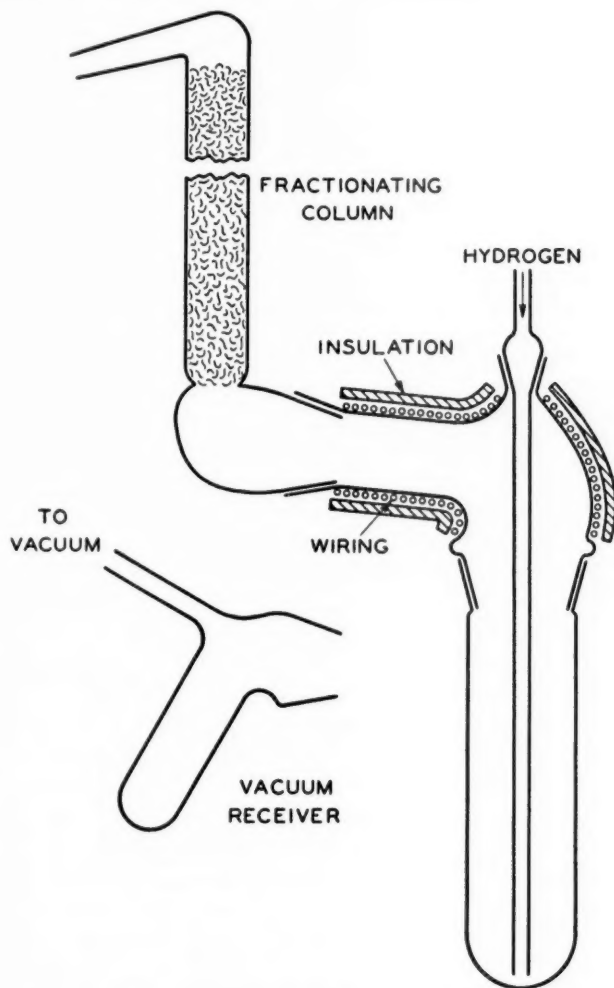


Fig. 1.—Apparatus for preparation of small laboratory batches of polyesters.

#### CONTROL OF MELTING POINT

The high molecular linear polyesters which have received most attention in the literature are microcrystalline waxes. These have been described in the work of Lyeon and Adams<sup>5</sup>, Carothers and coworkers<sup>6</sup>, and Fuller and coworkers<sup>7</sup>.

Examples are polyethylene sebacate, melting point 74°, polyethylene succinate, m.p. 100°, polydecamethylene sebacate, m.p. 74°, polyhydroxy de-

canoate, m.p. 74–76°, etc. All of these materials would be classified as plastics—that is, they are rigid solids at room temperature.

In contrast to them, however, polypropylene sebacate and polypropylene succinate are amorphous balsamlike substances which show no tendency to crystallize at room temperature<sup>8</sup>. This effect of a lowering of melting point by aliphatic substituents on the chain is common in polymer chemistry—for example, the relation of polyisobutylene to polyethylene, and the methylated polyamides to the unmethylated<sup>9</sup>—and it is this effect which makes possible the production of polyester rubbers. Actually polypropylene sebacate crystallizes slowly at lower temperatures and melts at about 10° C. Polypropylene succinate freezes to a glass at about -10° C. The copolyesters formed from the three components ethylene glycol, propylene glycol, and sebacic acid all have melting points between those of polyethylene sebacate and polypropylene sebacate. All ethylene-propylene succinates in which the proportion of propylene residues is more than 50 mole-per cent are completely amorphous at room temperature. Unless otherwise stated, all sebacates in this paper have an ethylene-propylene ratio of 20 to 80 mole-per cent, and all succinates a ratio of 50 to 50 mole-per cent.

Another method of controlling the melting point of polyesters for the purpose of making rubbery products is the use of sufficiently complicated mixtures of dibasic acids or glycols without any side chains. When a mixture of several dibasic acids is reacted with ethylene glycol, soft, low melting products may be obtained. The method is of limited application because of the small number of suitable intermediates available, but it makes possible the use of certain acid mixtures resulting from the oxidation of oils, fats, etc. For the purposes of this paper discussion will be confined to ethylene-propylene esters of succinic, adipic, sebacic, phthalic, and maleic acids.

### VULCANIZATION

The term vulcanization, as applied to rubber, may be defined as the introduction of primary valence cross-links between essentially linear polymer chains. To make the polyester gums useful as rubbers, it was necessary to find some method of introducing cross-links in a controlled manner. The esters so far described are completely saturated and hence cannot be vulcanized by the conventional methods which are based on the reaction of sulfur or sulfur compounds with polymers containing ethylenic double bonds. However, it was learned early in the polyester work that saturated ester chains are subject to attack by free radicals. One of the results of the reaction is the linking of two ester molecules, presumably through the carbon atoms alpha to the carbonyl group. Regardless of the mechanism, which has not been too well investigated, the empirical fact is that attack by free radicals constitutes an admirable method of vulcanizing saturated polyester rubbers.

A convenient source of free radicals for this vulcanization is the decomposition of benzoyl peroxide. A saturated ethylene propylene sebacate polyester requires about 4 per cent of its own weight of benzoyl peroxide for optimum cure. A saturated succinate requires about 10 per cent. In all cases the peroxide is added to the gum on a rubber mill, and the mix is cured in much the same manner as are conventional rubber compounds. The decomposition point of benzoyl peroxide is about 107° C, and any temperature above that is satisfactory for curing polyester rubber. Normally a temperature of 125° to 150° C is used. The cure is almost instantaneous and is not affected appre-

ciably by time or temperature. Thus the product can be heated for an hour at  $150^{\circ}\text{C}$  without overcuring, although 10 minutes at  $130^{\circ}\text{C}$  is adequate. Suitable sources of free radical other than benzoyl peroxide may also be used—for example, stearoyl peroxide or phenyl azide—but they appear to have no advantage, and in the case of the azides are even dangerous.

Although vulcanization of saturated polyesters can thus be accomplished by the use of 4 per cent or more of benzoyl peroxide, this has the disadvantage that it leaves in the rubber a fairly large amount of benzoic acid, which is one

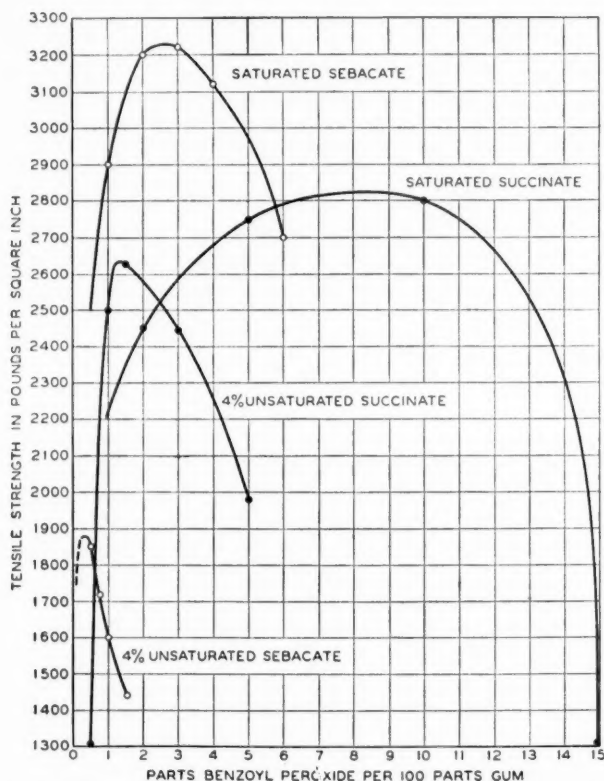


Fig. 2.—Tensile strength of various polymers loaded with 150 parts Mapico 297 as related to amount of benzoyl peroxide used in vulcanization.

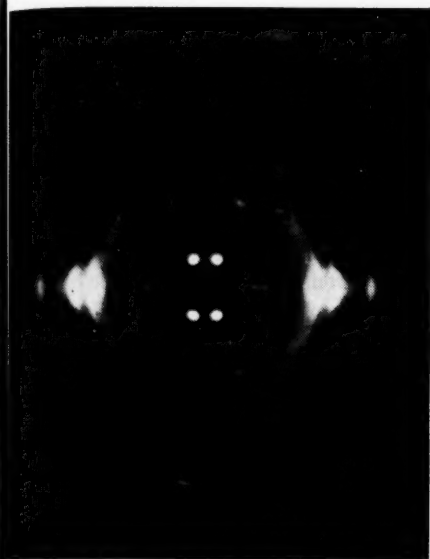
of the byproducts of the decomposition. The presence of acidic or alkaline substances materially damages the aging characteristics of esters and hence is undesirable. Efforts were therefore made to lower the amount of peroxide needed for optimum cure. It was soon found that replacement of a few mole per cent of the saturated dibasic acid in the original reaction mixture with an equivalent amount of maleic or other unsaturated acid facilitates markedly the vulcanization of the resulting product. Thus a polyethylenepropylene sebacate containing 3 mole-per cent maleic residues is well cured with only 1 per cent of its own weight of benzoyl peroxide. Corresponding succinates require about 2 per cent (Figure 2).

Polyesters containing 3 per cent unsaturation are still not vulcanizable by sulfur, but when the unsaturation is raised to about 15 per cent vulcanization can be obtained with sulfur and the usual organic accelerators. These facts suggest that sulfur vulcanization may require superimposition of double bonds in the adjacent molecules, whereas the peroxide type does not. The peroxide vulcanization of polymers containing unsaturation is effective at low peroxide concentration, presumably because of the greater ease of activation of the double bonds and resultant greater concentration of polymer free radicals.

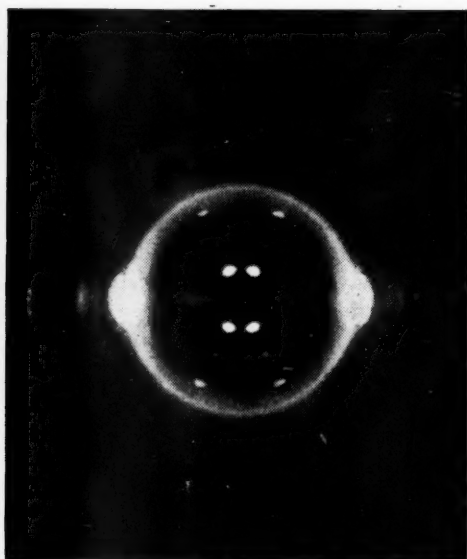
### PROPERTIES OF VULCANIZATES

The polyester vulcanizates look and feel like natural rubber, but, like many synthetic rubbers, the gum stocks usually have low tensile strength. However, a sample of polyethylenepropylene sebacate gum stock, which before vulcanization had been fractionated by solvents to remove low molecular-weight portions, showed a tensile strength of 1800 pounds per square inch when pulled at the rate of 20 inches per unit. As Figure 3 shows, considerable crystallization occurs during this stretching process. This figure represents x-ray patterns of the unstretched (*C*) and fully stretched (*D*) fractionated polymer which contained 80 mole-per cent propylene and 20 mole per cent ethylene glycol reacted with sebacic acid<sup>10</sup>. For comparison, a 50-50 polymer of the same components is shown unstretched in Figure 3*B*, and a fiber pattern of pure polyethylene sebacate is shown in Figure 3*A*. It is evident that, as propylene groups with their appended methyl groups are added, an increased amount of amorphous scattering occurs in the x-ray pattern. Apparently, in the solid, regions of low degree of order are being produced as more methyl is introduced. When still higher percentages are reached (80 per cent) the polymer is entirely amorphous at room temperature. When the sample is cooled to about 35° C and allowed to stand, even this higher substituted material will crystallize; this shows that the methyl groups lower the melting point of the polymer but do not seriously interfere with the chain packing. When the 80 per cent propylene polymer is vulcanized, its crystallization temperature decreases still further (to approximately 20° C), as in the case of Neoprene. At room temperature (above about 20° C), therefore, it is necessary to stretch the 80 per cent polymer to induce crystallization. The degree of ordering on stretching is high (Figure 3*B*), and the only effect of the methyl groups on the structure appears to be to expand slightly the dimensions perpendicular to the chains to conform to the greater space requirements. Thus in the pure polyethylene sebacate these dimensions are 4.18 Å. and 3.75 Å., whereas in the 80 per cent propylene copolyester they are 4.20 Å. and 4.00 Å., respectively. There is in addition a decrease in intensity of the original 3.75 Å. reflection. The fiber periods in the two cases are identical (16.9 Å.), as would be expected from the chain structures. When the specimen of Figure 3*B* is relaxed, the pattern of 3*A* is again obtained; this shows that the effect is reversible.

This observed crystalline behavior of the 80 per cent propylene polyester explains the high tensile strength observed in this particular gum stock. The rate of crystallization or ordering on stretch, however, is relatively slow<sup>10</sup> compared to natural rubber, so that on a rapid application of force the tensile strength is low. Thus for the best comparison of properties the polyester rubbers should be reinforced with pigments. The remainder of this discussion will deal with pigmented stocks.



A. 100% Ethylene



B. 50 Mole % ethylene, 50 mole % propylene

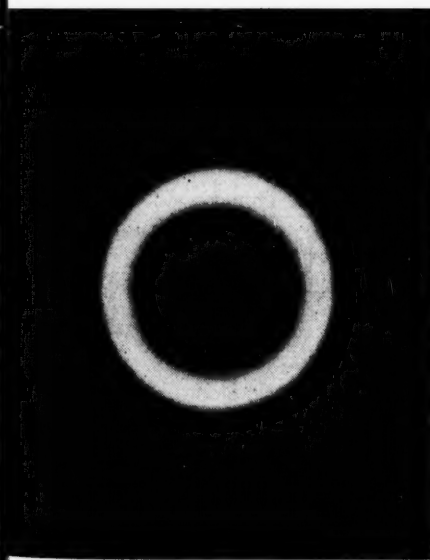
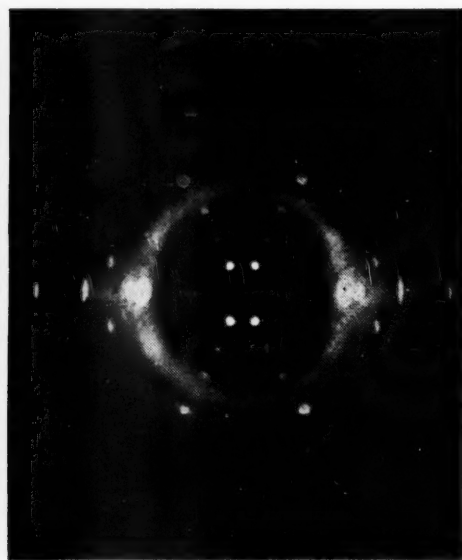
C. 20 Mole % ethylene, 80 mole % propylene  
(unstretched)D. 20 Mole % ethylene, 80 mole % propylene  
(stretched 600%)

FIG. 3.—X-ray patterns of sebacic acid polyesters at 25° C with fiber axes vertical.

The polyesters wet most pigments extremely well and are highly reinforced by those which are finely divided, although the use of certain ones of the available finely divided pigments is undesirable for other reasons. Carbon black, for example, cannot be used with benzoyl peroxide-cured stocks because they catalyze the decomposition of peroxide and prevent its vulcanizing action unless very large amounts are used, in which case the benzoic acid produced causes rapid hydrolysis of the vulcanizate. Zinc and magnesium oxides hydrolyze the ester rapidly and should never be used with it. The most satisfactory pigments for use with the polyesters appear to be the whittings, iron oxides, and clays, and of these Kalvan (a calcium carbonate) and Mapico 297 (an iron oxide) are outstanding. The tensile strength of properly loaded polyester rubbers ranges from 1600 to 3300 pounds per square inch, depending on type, and the elongations average between 300 and 600 per cent. The outstanding characteristic of the vulcanizates is good resistance to oil, ozone, light, and heat. This and other properties of polyester rubbers are functions of composition and structure. Some of these properties have been measured fairly accurately and will be discussed in the following paragraphs.

#### FACTORS AFFECTING TENSILE STRENGTH

*Pigment reinforcement.*—Figure 4 shows the relation of amount of loading to tensile strength for a 3 per cent unsaturated ethylene-propylene succinate loaded with Mapico 297. The strength rises steeply with increased loading and passes through a maximum. Similar curves are obtained for other pigments,

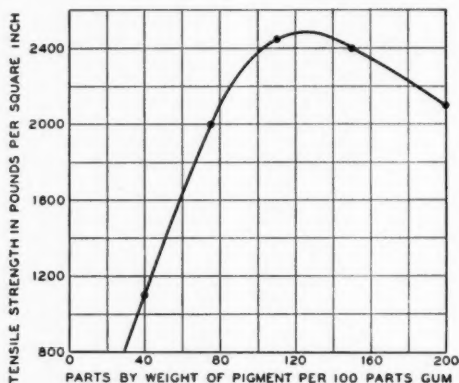


Fig. 4.—Tensile strength of 3% unsaturated ethylene propylene succinate as affected by amount of Mapico 297 incorporated.

but the maximum tensile strength obtainable varies from one pigment to another and appears to be related to the particle size of the pigment, as might be expected. For the finest pigments maximum tensile strength occurs at a volume loading of 25–30 per cent. The following table gives values of maximum tensile strength for several pigments in different particle sizes at optimum loading in 3 per cent unsaturated ethylene-propylene succinate polyesters:



	Tensile strength, lb./sq. in.
Calcium carbonates	
Whiting A	1200
Kalvan	2550
Iron oxides	
Iron oxide A	1100
Mapico 516	1750
Mapico 297	2400
Talc	
Coarse	900
Reground	1900

Of the two calcium carbonates shown, Kalvan is known to be much more finely divided than Whiting A<sup>11</sup>, and of the three iron oxides, Mapico 297 is much the finest<sup>12</sup>. The material designated "reground talc" was obtained by a further grinding operation on the sample called "coarse talc". Although it cannot be said that other factors are not also present, these results show clearly that reinforcement is a function of the particle size of the pigment. This is probably true for all rubbers when the pigment is truly dispersed. It is of interest that Mapico 297 and Kalvan confer almost as high a tensile strength on polyester rubbers as is usually found in carbon black-loaded GR-S stocks, and this suggests that, if they could be properly dispersed in GR-S, equally high tensiles might be obtained<sup>13</sup>.

*Molecular weight and molecular weight distribution.*—As with other rubbers, the tensile strength of the polyester rubbers is affected by the molecular weight of the polymer. This point has not been studied systematically, but in the course of the work polymers of different average molecular weights have been examined. Table I presents the tensile values on three saturated ethylene propylene sebacates.

TABLE I  
EFFECT OF AVERAGE MOLECULAR WEIGHT ON TENSILE  
STRENGTH OF POLYESTER RUBBERS

Sample designation	$\frac{\ln \eta_r}{c}$	$\overline{M}_w$	$\overline{M}_n$	Tensile strength, lb./sq. in.
GA 225	0.929	27,700	13,850	3100
GA 226	0.783	23,000	11,500	2915
GA 227	0.698	20,260	10,130	2450

The weight average molecular weights were calculated from solution viscosities with the equation (3):

$$\frac{\ln \eta_r}{c} = 0.31 \times 10^{-4} \overline{M}_w + 0.07 \quad (1)$$

where  $c = 0.4$  gram per 100 ml.

The number average molecular weights are assumed to be half the weight average values, in line with Flory's distribution curve<sup>14</sup>.

Further data were obtained by fractionating a sample of the polymer GA 227 (Table I) roughly in halves by suitable solvents and compounding and curing the high molecular weight half. The tensile strength of this vulcanizate was 3200 pounds per square inch. The low molecular weight half was so soft and sticky that it could not be compounded satisfactorily.

Although the data of Table I are not extensive, they show that variations in molecular weight, at least in the range indicated, have an important effect.

*Orderliness of chain structure.*—The high tensile strength of crystalline polyesters is to a large extent a result of the attractive forces between the polar groups. When rubbery polyesters are stretched to high elongations they crystallize like natural rubber, provided the orderly occurrence of repeating units has not been disturbed. The highest degree of order obtainable in a polyester rubber of the ethylene-propylene series is that in which a single dibasic acid is involved, such as the saturated sebacate or succinate. These polymers, when properly compounded and cured, have tensile strengths ranging from 2800 to 3200 pounds per square inch. When the orderly repetition of the units is disrupted by inclusion of another reactant as in copolymers, the polar groups in adjacent chains fail to coördinate, and tensile strength falls (Figures 5, 6, 7).

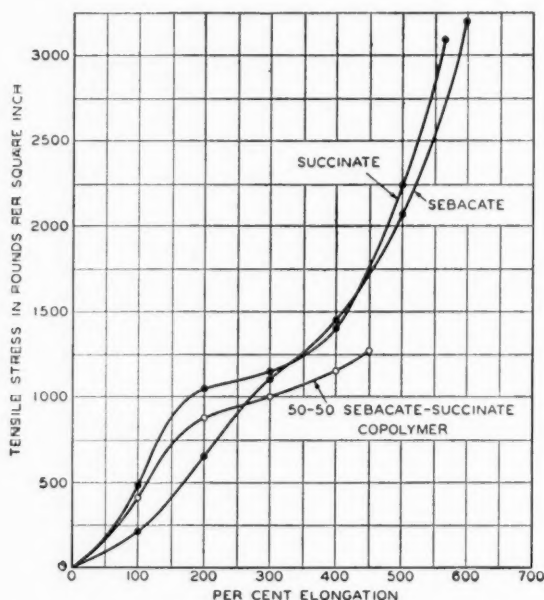


Fig. 5.—Stress-strain curves at optimum cure for various saturated polymers loaded with 150 parts Mapico 297.

This behavior is analogous to that of the linear copolyamides<sup>15</sup>. Examples of co-reactants which lower the tensile strength of sebacates are succinic and maleic acids. These, being four-carbon acids, alter the spacings of the polar groups along the chain. The effect of succinic and maleic, furthermore, is not the same, that of maleic being much the larger, as a comparison of Figure 8 with Figures 5, 6, and 7 shows. This difference probably reflects a concomitant lowering of chain length, which is a result of the reactivity of the double bond of the maleic residue. This reactivity inevitably introduces some cross linking during the period of preparation of the polymer, so that the limiting melt viscosity is reached at a lower average chain length. This, together with the disrupting effect of the cross-links, leads to lower tensile strength.

The effect of small proportions of maleate residues on succinate polymers is less pronounced, presumably because they are both four-carbon units, but it becomes quite large as the maleate content increases. This is demonstrated in Figure 9, which shows a plot of maximum tensile strength at optimum cure

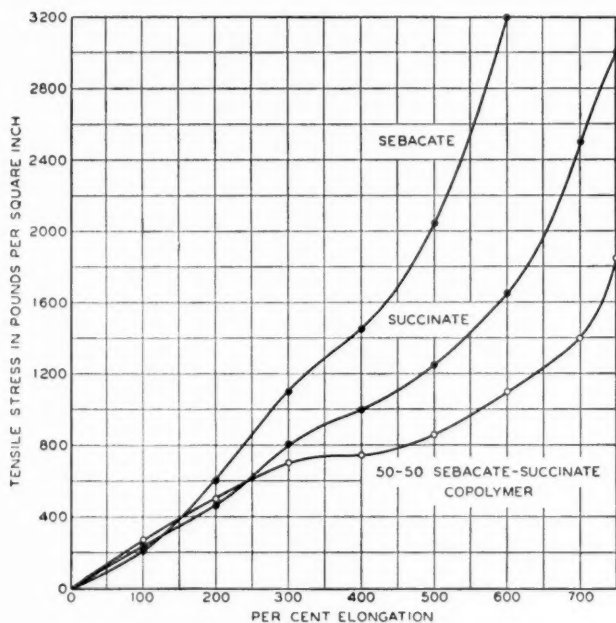


Fig. 6.—Stress-strain curves at optimum cure for various saturated polymers loaded with 75 parts Kalvan.

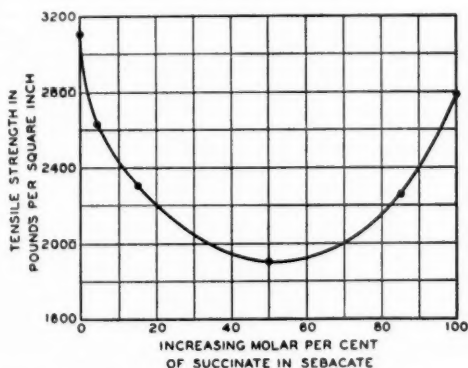


Fig. 7.—Maximum tensile strength at optimum cure of saturated sebacate-succinate copolymers loaded with 75 parts Kalvan.

against increasing maleate content. The strength is seen to fall off rapidly beyond about 4 per cent maleate, probably because of the decrease in effective chain length and cross-linking mentioned. Figure 8, in addition to the sebacate-maleate and succinate-maleate (the 4 per cent unsaturation is from

maleate), also presents data on a sebacate-succinate-maleate copolymer and on a mixture obtained by adding sebacate-maleate polymer to succinate-maleate polymer in equal amounts. The mechanical mixing of the two poly-

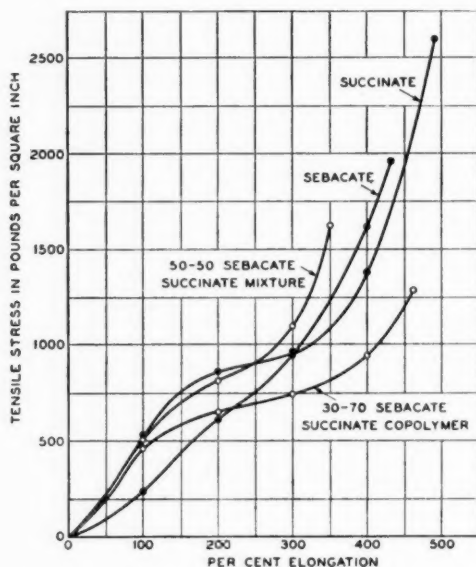


Fig. 8.—Stress-strain curves at optimum cure for various 3% unsaturated polymers loaded with 150 parts Mapico 297

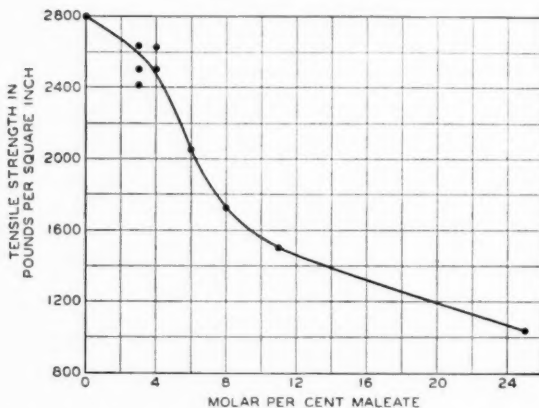


Fig. 9.—Maximum tensile strength at optimum cure of succinates loaded with 150 parts

mers lowers the tensile strength below that of either pure component but still does not have so pronounced an effect as copolymerizing the same intermediates.

*State of cure.*—It was pointed out earlier that polyesters do not overcure with time or heat, but that degree of cure is controlled by the amount of unsaturation and amount of peroxide used. Figure 2, which was cited in the

discussion of vulcanization, illustrates clearly the effect of stage of cure on tensile strength. Overcuring lowers tensile rapidly, particularly in unsaturated polymers. This is characteristic of most rubbers and is probably the result of the hampering effect of cross-links on chain orientation. The chains in a highly cross-linked sample—that is, in an overcure—are not able to reach the high elongations which permit good chain alignment (and result in wider distributions of the applied stress) and therefore are more easily broken.

### BRITTLE TEMPERATURE

Other rubbery systems, such as copolymers of butadiene with styrene, butadiene with acrylonitrile, and butadiene with dichlorostyrene, have given ample evidence that the brittle temperature of the finished polymer is a function of the concentration of polar groups present in it. The work with polyester rubbers adds to the weight of this evidence and furthermore indicates that orderliness of structure, at least in the amorphous state, is not important with regard to this property.

The brittle temperature of ethylene propylene sebacate is about  $-47^{\circ}\text{C}$ , that of the succinate is about  $-12^{\circ}\text{C}$ , and sebacate-succinate copolymers have intermediate values lying on a curve which is only slightly concave upward (Figure 10). Furthermore the adipate containing two carbonyl groups in a

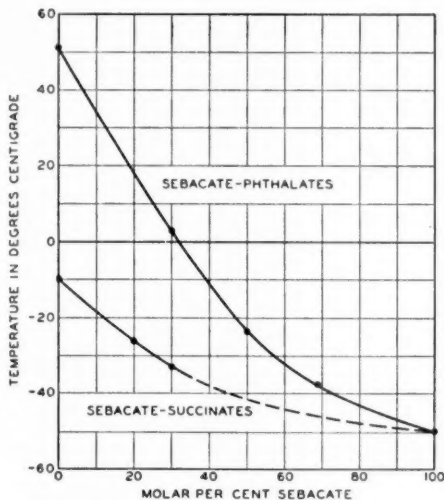


FIG. 10.—Brittle points of sebacate-succinate and sebacate-phthalate copolymers loaded with 150 parts Mapico 297.

repeating unit of 186 has almost exactly the same brittle temperature as a sebacate-succinate containing the same number of carbonyl groups per unit weight (this polymer results from two moles of succinic acid and one mole of sebacic acid), although the orderliness of structure is far greater in the adipate than in the sebacate-succinate copolymer. The brittle temperature of ethylene propylene phthalate is above room temperature, and the phthalate-sebacate copolymers fall on a smooth curve, which again is only slightly concave upward and shows no significant effect of the greater disorder of the copolymer.

## OIL RESISTANCE

The resistance of a rubber to the swelling action of various hydrocarbon oils and solvents has been shown by experience on the Buna N type rubbers of varying acrylonitrile content to be a function of the concentration of the polar nitrile groups in the polymer. Thus a rubber which is 40 per cent acrylonitrile is much more resistant than one containing 18 per cent. The same rules hold for the polyester rubbers, in which the polar group is carbonyl. Succinate polymers are extremely resistant to the swelling action of hydrocarbon oils and gasoline, and even pure toluene produces a linear expansion of only about 10 per cent. Adipates and sebacates are affected proportionately more in toluene or in aromatic gasoline, but are not attacked by mineral oils. As with brittle points the property appears to be a function of composition alone and is not related to orderliness of structure. Thus, as with the brittle point, the adipate is swollen by a given type of gasoline to the same extent as is a succinate-sebacate copolymer which has the same number of carbonyl groups per unit length.

TABLE II  
OIL RESISTANCE OF POLYESTER RUBBERS

Polyester composition		% Change in length after 48 hr. in	
Polymer	Pigment or filler, parts	100 octane gasoline	40% aromatic gasoline
Succinate	Clay, 50	0.0	0.7
Adipate	Clay, 50	1.5	6.0
Sebacate	Clay, 50	6.0	20.0
Succinate	Iron oxide, 150	0.0	0.0
Sebacate-phthalate, 70-30	Iron oxide, 150	3.0	6.0
Succinate	Carbon black*, 60	-1.5	0.0
Succinate	Iron oxide*, 150	-1.5	-1.5
Sebacate-succinate, 20-80	Clay, 50	0.0	3.0
Sebacate-succinate, 30-70	Iron oxide, 150	0.7	7.0

\* Cured with 9 parts benzoyl peroxide.

Table II gives the per cent change in length of strips of various compounds after 48 hours immersion in gasoline. The original dimensions of the strips were  $\frac{1}{16} \times \frac{1}{4} \times 2$  inches. Change in the 2-inch dimension was used as the criterion of relative swell. Unless otherwise noted, the compounds consisted of 100 parts polymer, the stated amounts of pigment, and 1.5 parts benzoyl peroxide.

## DIELECTRIC PROPERTIES

The electrical properties of solid linear polyesters have been reported by Yager and Baker<sup>16</sup>. The present rubberlike polyesters having similar chemical composition exhibit somewhat analogous behavior. The lower intermolecular forces, particularly the reduced polar coördination as a consequence of substitution with its attendant steric disorder, however, result in dielectric constants and power factors, at the same temperature and frequency, which are higher than those shown by the solid linear polyesters. Also the effect of water absorption is greater. Typical dielectric properties are shown in the following table for clay-filled compounds.



	Days in water at 25° C	Power factor, %	Dielectric constant	D. C. resistivity, ohm-cm. (400 volts)
Succinate	0	1.30	8.20	$5 \times 10^{12}$
	7	17.2	25.1	$2 \times 10^9$
Sebacate	0	0.536	5.72	$9.8 \times 10^{12}$
	7	3.8	10.7	$6.5 \times 10^{11}$

The better electrical behavior of the more hydrocarbonlike sebacate polyester is evident.

### FACTORS AFFECTING USEFUL LIFE

The properties discussed so far are the original properties characteristic of new samples. It is appropriate now to see what factors act to degrade these properties with time. The atmospheric agents which are known to deteriorate natural rubber rapidly are ozone and oxygen, the attack of the latter being accelerated by heat and light<sup>17</sup>. It is recognized that the chief action of ozone is attack of double bonds, and since vulcanized polyesters are substantially saturated these rubbers are quite resistant to ozone, as would be expected. In this regard they rank with Butyl rubber, Thiokol, and Neoprene. The other enemies of natural rubber, however, also act on polyesters, and in addition the latter are subject to hydrolysis, which is not directly a factor with natural rubber.

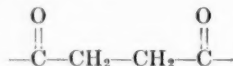
*Oxidation accelerated by heat.*—The deterioration of natural and most synthetic rubbers with heat (short of pyrolysis) is largely an oxidative effect. This is evident from the fact that the action proceeds from the outside and gradually works to the center of a test piece. Thermal oxidation tests which have been run on polyester rubbers include the standard oxygen bomb aging at 70° C and air oven aging at 100° C. Data obtained in these tests on compound M 165 (a sebacate—3 per cent maleate polymer) are shown in Table III.

TABLE III  
AGING OF SEBACATE-MALEATE POLYESTER RUBBER  
CURED 10 MINUTES AT 150° C

	Air oven at 100° C			
	0	7 days	14 days	28 days
Shore A hardness	66	..	63	63
Tensile strength, lb./sq. in.	1735	1585	1620	1435
	380	330	330	315
	Oxygen bomb at 70° C and 300 lb./sq. in.			
	0	2 days	4 days	10 days
Tensile strength, lb./sq. in.	1735	1655	1640	1625
Elongation, %	380	355	350	365
Composition of M 165				
Ethylene propylene sebacate maleate (20-80-97-3)				
Kalvan				
Luperc A*				
				100
				75
				4.35
				Total 179.35

\* Luperc A is a suspension of benzoyl peroxide on calcium sulfate. Peroxide content is about 23 per cent.

One of the most significant aspects of these results is the fact that hardness does not increase with heat aging. This again reflects the low unsaturation of these rubbers. The usual ultimate effect of thermal oxidation on polyester rubbers is to bring about reversion. Hardness and brittleness result only in polymers containing about 10 per cent or more unsaturation or in sebacates subjected to high temperature (150° C). In spite of their stability at 100° C the sebacates deteriorate rapidly at 150° in air. The succinates, however, are quite resistant to oxidation even at 150°, and some samples have been found to retain a high proportion of their original tensile strength, with no increase in hardness, after 30 days at this temperature. This phenomenal resistance to oxidation of succinates as compared to sebacates and adipates suggests that there is a special merit in the grouping:



and that if polymers could be built with this structure and without the ester link (the great weakness of polyesters) they would have superior stability. The tests reported here are on materials which do not have the protection of antioxidants (since antioxidants inhibit peroxide vulcanization), a fact which makes this stability seem even more remarkable. By external application of antioxidants, such as by diffusion from solutions, it is possible to improve the behavior of both the sebacate and succinate compounds. The sebacate gains considerably by this treatment.

*Oxidation accelerated by light.*—With regard to outdoor exposure, a serious degradation influence for polyester rubbers is light-activated oxidation, which causes surface checking on light colored samples. This action is stopped to a large extent by shutting off the light with a pigment of high opacity such as iron oxide, and the uniformly better outdoor aging of samples containing iron oxide as compared with those containing calcium carbonate is evidence of this. This difference in aging between white and red samples in identical polymers is illustrated in Table IV.

TABLE IV  
AGING POLYESTER RUBBERS CONTAINING DIFFERENT FILLERS

	White*		Red	
	T.S.†	E.‡	T.S.	E.
3% unsaturated succinate				
Original	2600	500	2560	480
After 3½ years outdoors	1075	400	1775	530
4% unsaturated sebacate				
Original	1450	390	1650	400
After 3½ years outdoors	425	210	1100	400

\* The white samples all contain 75 parts Kalvan and the red samples 150 parts Mapico 297. All samples were given optimum cure.

† T.S. = tensile strength, pounds per square inch.

‡ E. = elongation, per cent.

It is to be expected that samples of different structures may vary in their resistance to oxidation. The most striking examples of this encountered in the polyester work are in polymers containing diethylene or dipropylene glycol as a component. These polymers are oxidized much more rapidly than are similar polymers made of ethylene or propylene glycols and testify to the ease of

attack on the ether linkage in such structures. This is true both in oven aging and in outdoor exposures. It should be emphasized that these polymers are without benefit of antioxidant.

*Hydrolysis.*—Susceptibility to hydrolysis is a serious defect of polyester rubbers. Polyesters are not resistant to acid or alkali or to hot water or steam, and, as a matter of fact, immersion in water at 60°, 80°, or 100° C is a convenient accelerated test for studying the effects of various factors on rate of hydrolysis. Samples of 3 per cent unsaturated sebacates lose their shape after about 72 hours of continuous immersion in boiling water, and succinates, being more hydrophilic, break down similarly in about 24 hours. Immersion of water at 60° is a slower and more discriminating test for succinates, and 80° water is convenient for sebacates. Hydrolysis of vulcanized polyester rubbers invariably manifests itself in a lowering of modulus and an increase in elongation; in other words, it has the effect of devulcanization or reversion. Therefore the progress of hydrolysis is easily followed by use of a simple test which measures the elongation of samples of standard size and length under a given fixed load. A reading is taken 10 seconds after the load is applied, and the sample is then released and can be used in further tests. From the hot water tests several facts stand out.

1. Sebacates, presumably because of their more hydrocarbon nature, are markedly more resistant to hydrolysis than succinates; samples of the one, for example, are better after 13 days in water at 80° C than corresponding samples of the other after 4 days.

2. Other things being equal, the greater the original per cent unsaturation (and therefore presumably the more highly cross-linked after vulcanization) the more resistant is the polymer to hydrolysis. For example, a 4 per cent unsaturated sebacate after 13 days in 80° water is equal to a saturated sebacate containing the same loading after about 4 days. Similarly a 14 per cent unsaturated succinate after 27 days in 60° water is better than a 3 per cent unsaturated succinate of the same loading after 18 days.

3. Pigments which are able to neutralize acid (such as calcium carbonate) confer the greatest resistance to hydrolysis.

Although hot water thus rapidly hydrolyzes polyesters, neutral water at room temperature is not a serious hazard, and outdoor exposure to rain is really beneficial since it tends to leach out and wash away the benzoic acid left from vulcanization. It is interesting in this connection that, whereas iron oxide is the best pigment for outdoor use because of its opacity, polymer samples kept indoors retain their properties much better if they are loaded with calcium carbonate. It follows, then, that for general uses samples should contain both calcium carbonate and iron oxide. When properly compounded, polyester rubbers are far less seriously damaged by atmospheric moisture than are unsaturated hydrocarbon rubbers by atmospheric ozone. Table V gives original and aged tensile strength and elongation measurements on samples of succinate-maleates of varying unsaturation, all loaded with 150 parts of Mapico 297 iron oxide and each given optimum cure.

These changes in properties include the combined effects of oxidation and hydrolysis, and demonstrate the superior aging of unsaturated samples.

All the available test data indicate that, for uses where hydrolysis is expected to be the most serious degradative factor, an unsaturated sebacate would be expected to give the best results, and where oxidative influences predominate, unsaturated succinates would be chosen. Tables IV and V appear

TABLE V  
EFFECT OF AGING SUCCINATE-MALEATES OF VARYING UNSATURATION

	0% Unsatn.		3% Unsatn.		6% Unsatn.		8% Unsatn.		11% Unsatn.	
	T.S.*	E †	T.S.	E.	T.S.	E.	T.S.	E.	T.S.	E.
Original	2750	540	2560	480	2000	400	1600	340	1650	325
After 3½ years out- doors	Disinte- grated		1775	530	1675	430	1400	380	1150	330

\* T.S. = tensile strength, pounds per square inch.

† E = elongation, per cent.

to indicate that sebacates and succinates in outdoor exposure degrade at about the same rate, and this presumably means that in these conditions oxidation and hydrolysis are of about equal importance.

#### ACKNOWLEDGMENT

The authors are indebted to N. R. Pape for the x-ray pictures and to C. V. Lundberg for much of the physical testing.

#### REFERENCES

- Biggs and Fuller, *Chem. Eng. News* **21**, 962 (1943).
- Carothers and Van Natta, *J. Am. Chem. Soc.* **55**, 4714 (1933); Baker, Fuller and Heiss, *J. Am. Chem. Soc.* **63**, 2142, 3316 (1941); Fuller and Baker, *J. Chem. Ed.* **20**, 3 (1943).
- Carothers and Van Natta, *J. Am. Chem. Soc.* **55**, 4714 (1933); Flory, *J. Am. Chem. Soc.* **58**, 1877 (1936); Baker, Fuller and Heiss, *J. Am. Chem. Soc.* **63**, 2142, 3316 (1941).
- Shorland, *J. Am. Chem.* **57**, 115 (1935); Flory, *J. Am. Chem. Soc.* **62**, 2261 (1940).
- Lycan and Adams, *J. Am. Chem. Soc.* **51**, 3450 (1929).
- Carothers and Arvin, *J. Am. Chem. Soc.* **51**, 2560 (1929); Carothers and Hill, *J. Am. Chem. Soc.* **54**, 1559 (1932); Carothers and Van Natta, *J. Am. Chem. Soc.* **55**, 4714 (1933).
- Fuller and Erickson, *J. Am. Chem. Soc.* **59**, 344 (1937); Fuller and Frosch, *J. Am. Chem. Soc.* **61**, 2575 (1939); Baker, Fuller and Heiss, *J. Am. Chem. Soc.* **63**, 2142, 3316 (1941).
- Fuller, *Ind. Eng. Chem.* **30**, 472 (1938).
- Biggs, Frosch and Erickson, *Ind. Eng. Chem.* **38**, 1016 (1946).
- Baker, *Bell Labs. Record* **23**, 97 (1945); *RUBBER CHEM. TECH.* **18**, 632 (1945).
- Clark, Le Tourneau and Ball, *Ind. Eng. Chem.* **35**, 202 (1943).
- Columbian Carbon Co., "Red Oxide of Iron", 1941, p. 61.
- McMahon and Kemp, *Ind. Eng. Chem.* **36**, 735 (1944).
- Flory, *J. Am. Chem. Soc.* **58**, 1877 (1936).
- Baker and Fuller, *J. Am. Chem. Soc.* **64**, 2349 (1942).
- Yager and Baker, *J. Am. Chem. Soc.* **64**, 2164 (1942).
- Newton, *J. Rubber Research* **14**, 27 (1945); Crabtree and Kemp, *Ind. Eng. Chem.* **38**, 278 (1946).

# THE SOLUBILITY OF GASES IN ELASTOMERS \*

R. M. BARRER

CHEMICAL LABORATORIES, BEDFORD COLLEGE, UNIVERSITY OF LONDON,  
REGENTS PARK, LONDON, ENGLAND

*Introductory.*—Kinetic and statistical methods have led to the progressive interpretation of heterogeneous equilibria. Adsorption of gases in monolayers<sup>1</sup>, interstitial or zeolitic sorption of a volatile component<sup>2</sup>, multilayer persorption in gels<sup>3</sup>, and in colloids such as wool<sup>4</sup>, have all proved amenable to fairly precise treatments. The further development of these methods may clarify an increasing range of gas-colloid equilibria, typical among which are gas-elastomer systems. The group of elastic nonpolar polymers shows a considerable capacity to sorb nonpolar gases, but for these gases above their critical points the sorption isotherm has not so far been calculated, in spite of the intrinsic interest and practical importance of the phenomenon. An attempt to calculate the solubility by assuming the gas molecules to enter preëxisting holes in the elastomer gave results not in accord with experiment<sup>5</sup>. The present paper, however, derives a satisfactory sorption isothermal for permanent gases in elastomers based on the statistical thermodynamics of monomer-polymer mixtures, and compares experimental with calculated solubilities and isothermals.

*Distinction between the BET and the Present Isothermal.*—For sorption in gel and colloidal sorbents in which two kinds of sorption site coëxist, the isotherm often has a characteristic sigmoid form, which is well represented by the isotherm first deduced by Brunauer, Emmett and Teller by a kinetic argument<sup>6</sup>. The form of the isotherm derives from an entropy of mixing term, in which the sorbate molecules are distributed between the two types of sorption site in such a way as to minimize the energy. In a chemically homogeneous nonpolar elastomer, such as polyisoprene, there is no reason to suppose more than one type of sorption site. Therefore, although the BET isotherm can simulate the gas-rubber isotherm in curving away from the pressure axis<sup>7</sup>, the physical explanation of the form of the gas- or vapor-rubber isotherm cannot be that underlying the BET isothermal.

*Basis of the present treatment.*—An alternative explanation of gas-rubber solubilities and isotherms may be based on recent treatments of the statistics of monomer-polymer mixtures. Here the entropy of mixing term is obtained by finding the number of ways of distributing monomer molecules and polymer chains on an array of lattice sites all of one kind, each site having<sup>8</sup> a coördination number  $z$ . Each site may be occupied by a monomer molecule or by a segment of the polymer chain approximately equal in volume to that molecule. If there are  $n$  of these segments per polymer molecule, and the volume fractions of sorbed molecules and elastomer are  $v_0$  and  $v_r$ , respectively, successive treatments have given for the partial molal free energy of mixing of monomer with polymer:

$$\mu = RT/\beta[\ln v_0 + (1 - 1/n)v_r] \quad (\text{Flory})^9 \quad (1)$$

\* Reprinted from the *Transactions of the Faraday Society*, Vol. 43, parts 1-2, pages 3-10, January-February 1947.

( $\beta$  is the number of sorbed molecules replaceable by one segment of a rubber molecule):

$$\mu = RT[\ln v_0 + g_0(1 - 1/n)v_r] \quad (\text{Huggins})^{10} \quad (2)$$

where

$$g_0 = 1 + \sum_{i=1}^{\infty} \frac{1}{i} \left( \frac{2v_r}{z'} \right)^{i-1} \quad (2a)$$

( $z'$  is very nearly the coördination number  $z$ ):

$$\mu = RT [\ln v_0 - z/2 \ln \{1 - (1 - 1/n)2v_r/z\}] \quad (\text{Miller})^{11} \quad (3)$$

$$\mu = RT \left( \ln v_0 - z/2 \ln \{1 - (1 - 1/n)2v_r/z\} + z/2 \ln \frac{(\beta + 1) - 2x}{(1 - x)(\beta + 1)} \right) \quad (\text{Orr})^{12} \quad (4)$$

where

$$\beta = \{1 + 4x(1 - x)(e^{2w/zkT} - 1)\}^{\frac{1}{2}} \quad (4a)$$

$$x = \frac{\frac{nz + 2n + 2}{nz} \cdot v_r}{\frac{nz + 2n + 2}{nz} \cdot v_r + v_0} \quad (4b)$$

$$w = \frac{z}{2} (2w_{\alpha\beta} - w_{\alpha\alpha} - w_{\beta\beta}) \quad (4c)$$

the energy of interaction between two sorbed molecules being  $w_{\alpha\alpha}$ , between two rubber segments  $w_{\beta\beta}$ , and between a sorbed molecule and a rubber segment  $w_{\alpha\beta}$ ; and finally:

$$\mu = RT[v_0/\bar{n} + \ln v_0 + z/2 \ln (1 - 2/zv_r)] \quad (\text{Scott and Magat})^{13} \quad (5)$$

where  $\bar{n}$  is the number of segments in the number average molecular-weight polymer molecule.

Orr<sup>12</sup> pointed out that Miller's and Huggins' formulas if expanded term by term are virtually identical; while Flory's equation follows from those of Huggins or Miller on setting  $z = \infty$ . Since  $z$  cannot be  $\infty$ , Flory's equation may for present purposes be omitted<sup>14</sup>. These three equations and Equation (5) all assume random mixing and zero heat of mixing; Orr's equation, however, covers random mixing modified by non-zero energies  $w$  as given in Equation (4c). Equation (5) allows for heterogeneity of the polymer in respect of molecular weight. The effect of heterogeneity embodied in the term  $v_0/\bar{n}$  is small, and since  $n$  in Equations (2), (3) and (5) is large, all three are substantially identical. The equation of Miller will accordingly be used for random mixing with negligible energy  $w$ , and the equation of Orr when random mixing is modified by appreciable values for  $w$ . Even this equation, however, may be inadequate when  $w$  deviates considerably from zero, e.g., for methanol in rubber<sup>15</sup>.

*Procedure for determining the solubility of gases in elastomers.*—The following procedure is valid for a gas above its critical temperature, and leads, as a special case, to the vapor-elastomer isotherm.

Consider the isothermal transfer of a mol of gas from the gas phase where there are  $n_1$  molecules per cc. to an infinite amount of gas-elastomer mixture.



Then the molar free energy of the gas is:

$$A_g = RT \ln n_1 \frac{h^3}{(2\pi m k T)^{3/2}} \cdot \frac{1}{j_A(T)} \quad (6)$$

where  $h$  = Planck's constant,  $k$  = Boltzmann's constant,  $m$  = mass of the gas molecule, and  $j_A(T)$  = the partition function for all integral degrees of freedom of the molecule. The Helmholtz free energy of a mole of gas in the gas-elastomer mixture is numerically equal to the chemical potential,  $\mu_3$ , of the gas and is made up of three terms. The first is an energy,  $-\chi$ , where  $\chi$  is the least energy required to remove a mol of gas from the solution to the gas phase<sup>16</sup>. Then there is a free energy term corresponding to the partition function  $j(T)$  for the internal degrees of freedom of the sorbed molecule and its degrees of freedom relative to its new environment in the mixture. Finally there is the configurational free energy term discussed in the section on the "Basis for mixing sorbed molecules and polymer". Adding, one obtains:

$$\mu_s = -\chi + RT \ln \frac{1}{j(T)} + \mu \quad (7)$$

At equilibrium:

$$\Delta A = \mu_s - A_g = 0 \quad (8)$$

so that, substituting Equations (6), (7) and (3) (or (4)) in Equation (8) one obtains:

$$RT \ln n_1 \frac{h^3}{(2\pi m k T)^{3/2}} \frac{1}{j_A(T)} = -\chi + RT \ln \frac{1}{j(T)} + RT \ln \frac{v_0}{\{1 - (1 - 1/n)2v_r/z\}^{z/2}} \quad (9a)$$

and

$$RT \ln n_1 \frac{h^3}{(2\pi m k T)^{3/2}} \frac{1}{j_A(T)} = -\chi + RT \ln \frac{1}{j(T)} + RT \ln \frac{v_0}{\{1 - (1 - 1/n)2v_r/z\}^{z/2}} + RT \ln \left\{ \frac{\beta + 1 - 2x}{(1 - x)(\beta + 1)} \right\}^{z/2} \quad (9b)$$

The problem now reduces to the evaluation of  $j(T)$  in Equation (9).

*Isotherms corresponding to Equation (9).*—First nearly spherical sorbed molecules which may be considered to rotate freely in the mixture as in the gas phase will be considered. These molecules, enmeshed in the polymer, must behave relative to their environment as oscillators. Moreover the weak interactions with neighboring polymer segments are unlikely to modify internal degrees of freedom, the partition function for which is accordingly still  $j_A(T)$ . Thus:

$$j(T) = j_A(T) \left( \frac{kT}{h\nu} \right)^3 \quad (10)$$

Substitution of Equation (10) in Equations (9a) and (9b) then the isotherms for negligible  $w$  and finite  $w$ , respectively. Thus in the former case:

$$\frac{v_0}{\{1 - (1 - 1/n)2v_r/z\}^{z/2} \cdot n_1} = K = \left( \frac{kT}{2\pi m} \right)^{3/2} \cdot \frac{1}{\bar{v}^3} \cdot e^{\chi/RT} \quad (11)$$

whence recalling that  $\frac{\partial \ln K}{\partial T} = \frac{\Delta U}{RT^2}$ , one finds:

$$\frac{v_0}{\{1 - (1 - 1/n)2/z \cdot v_r\}^{z/2} \cdot n_1} = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \cdot \frac{1}{\bar{v}^3} \cdot e^{(-\Delta U + \frac{1}{2}RT)/RT} \quad (12)$$

When permanent gases are sorbed by elastomer at low or moderate pressures, the solution is usually very dilute so that  $v_0 \ll 1$  and  $v_r = 1$ . Then

$$\frac{v_0}{n_1} = \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{1}{\bar{v}^3} e^{(-\Delta U + \frac{1}{2}RT)/RT} [1 - 2/z]^{z/2} \quad (13)$$

and gas-elastomer systems then obey Henry's law. This low pressure behavior is common to the Langmuir, the BET, and the present isothermal, and is well substantiated by experiment. Finally one notes that, in the case of systems at constant pressure, substitution of  $p = n_1 kT$  in (12) gives:

$$\frac{v_0}{\{1 - (1 - 1/n)2/z \cdot v_r\}^{z/2} \cdot p} = \frac{1}{(kT)} \cdot \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{1}{\bar{v}^3} e^{(-\Delta H + \frac{1}{2}RT)/RT} \quad (14)$$

When nonspherical molecules, *e.g.*, *n*-paraffins, are sorbed by elastomers, the principal rotations, as well as translational degrees of freedom may be converted to vibrations. Isotherms corresponding to several kinds of mobility of the sorbed molecules in their environment are illustrated for zero *w* in Table I<sup>7</sup>. The conversion of rotations into vibrations when the gas molecule

TABLE I  
SOLUBILITY CONSTANTS FOR GASES IN ELASTOMERS

Type of movement executed in mixture by sorbed molecule	Solubility constant $K = \frac{v_0}{[1 - (1 - 1/n)2/z \cdot v_r]^{z/2} p}$	Equation No.
(1) Freely rotating oscillators.	$K = \frac{1}{kT} \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{1}{\bar{v}^3} e^{(-\Delta H + \frac{1}{2}RT)/RT}$	14
(2) Oscillators with one principal rotation also converted to a vibration.	$K = \frac{1}{kT} \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{1}{\bar{v}^3} \left(\frac{kT}{8\pi^2 I_1}\right)^{\frac{1}{2}} e^{(-\Delta H + RT)/RT}$	15
(3) Oscillators with two principal rotations also converted to vibrations.	$K = \frac{1}{kT} \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{1}{\bar{v}^3} \frac{kT}{8\pi^2 I_1 I_2} e^{(-\Delta H + \frac{3}{2}RT)/RT}$	16
(4) Oscillators with all three principal rotations converted to vibrations.	$K = \frac{1}{kT} \left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}} \frac{1}{\bar{v}^3} \left(\frac{kT}{8\pi^2 I_1 I_2 I_3}\right)^{\frac{1}{2}} e^{(-\Delta H + 2RT)/RT}$	17

is sorbed has a much smaller influence on gas-elastomer equilibria than has conversion of translations<sup>2</sup>.

If a vapor is sorbed by an elastomer, Equation (14) simplifies because as  $p \rightarrow p_s$ ,  $v_0 \rightarrow 1$  and  $v_r \rightarrow 0$ , then  $K = 1/p_s$ . Accordingly Equation (14) becomes for large *n*:

$$\frac{v_0}{[1 - 2/z \cdot v_r]^{z/2}} = p/p_s \quad (14a)$$

Moreover, for high polymers, where  $n$  is very large, unity may replace  $(1 - 1/n)$  in all the equations. Figure 1 (a), Curves 1, 2 and 3, then shows isothermals of  $v_0$  against  $p/p_s$  calculated from: (14a) when  $z = \infty, 6$  and 4. For the physically probable values of  $z = 6$  or 4 the isotherms are strongly concave towards the axis of  $p/p_s$ .

Figure 1 (b) shows the same isotherms with  $v_0/v_r$  as ordinate since this conforms closely with the usual method of expressing sorption data when using Langmuir or BET isotherms. Figure 1 (b) also give typical Langmuir and BET isotherms.

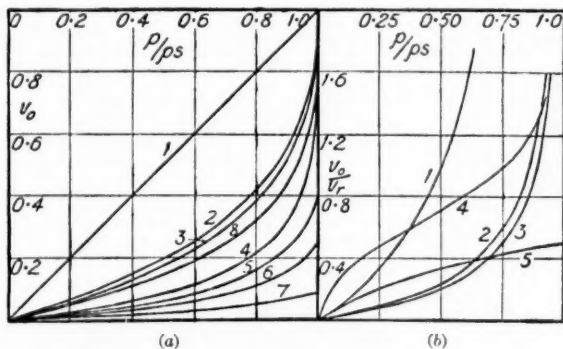


Fig. 1(a).—Curves 1, 2 and 3: isotherms according to Equation 14a, with  $z = \infty, 6$  and 4, respectively. Curves 4, 5, 6 and 7: isotherms according to Equation 19, with  $z = 4$  and  $w = 0.81 kT, 121, kT, 1.386 kT$ , and  $2kT$ , respectively. Curve 8: isotherm according to Equation 20, with  $\mu = 0.51$ .

Fig. 1(b).—Curves 1, 2 and 3: isotherms corresponding to curves 1, 2 and 3 of Figure 1 (a), using as ordinate  $v_0/v_r$  = volume of vapor sorbed per unit volume of elastomer. Curves 4 and 5: Langmuir and BET isotherms with same initial slope as curve 1.

#### Comparison with experiment: solubility of permanent gases in rubbers.—

Observed solubilities of permanent gases in rubbers are small at normal pressures, and the heats of sorption are of the same order as, or less than, the latent heats of condensation of the gases themselves below their critical temperatures<sup>18</sup> (see Table II). It is therefore probable that  $w$  (Equation (4c)) is very small, so Equation (13) or its constant pressure analogue should be valid. The term  $(1 - 2/z)^{z/2}$  does not vary greatly for probable values of  $z$  ( $6 > z > 4$ ), and the mean frequency  $\bar{\nu}$  corresponding to weak van der Waals interactions between solute and environment should be in the infrared ( $\sim 10^{12}$  sec.<sup>-1</sup>). Since  $\bar{\nu}$  is not known independently, however, the best test of Equation (13) is to determine the values of  $\bar{\nu}$  for which experimental and calculated  $v_0$  agree (Table II, column 4). The mean frequencies correspond as predicted to thermal vibrations in the infrared ( $\sim 10 - 40\mu$ ). The results are consistent among themselves,  $\bar{\nu}$  being greatest for the light molecule  $H_2$  and least for the heaviest molecule, A; moreover for a given solute  $\bar{\nu}$  does not change much for a series of elastomers. One may conclude that the theory is capable of predicting and interpreting the solubility of permanent gases in elastomers.

**Comparison with experiment: isotherms of vapors completely miscible with rubber.**—Data with which to test the isotherm of Equation (14a) are few in number<sup>19</sup>. An outstanding exception is the benzene-rubber system for which complete vapor pressure-composition data are available<sup>20</sup>.

In the Henry's law region of sorption one sees from Equation (14a) that:

$$v_0 = p/p_s(1 - 2/z)^{z/2} \quad (18)$$

TABLE II  
TEST OF THE ISOTHERM FOR PERMANENT GASES IN ELASTOMERS

Gas	Elastomer	Volume fraction $v_0$ of gas dissolved at 300° K and 1 atm. <sup>18</sup>	Value of $\nu$ (sec. <sup>-1</sup> ) to give agreement between observed and calculated $v_0$	Experimental <sup>19</sup> sorption heat $\Delta H$ (cal. per mol.) $\pm 100$
H <sub>2</sub>	Vulcanized Neoprene	$6.25 \times 10^{-6}$	$3.3 \times 10^{12}$	-970
	Butadiene-acrylonitrile interpolymer	$3.11 \times 10^{-6}$	$3.2 \times 10^{12}$	-500
N <sub>2</sub>	Vulcanized Neoprene	$7.9 \times 10^{-6}$	$1.0 \times 10^{12}$	-1400
	Butadiene-acrylonitrile interpolymer	$8.2 \times 10^{-6}$	$1.1 \times 10^{12}$	-1700
	Butadiene-styrene inter- polymer	$1.32 \times 10^{-4}$	$0.77 \times 10^{12}$	-1000
	Butadiene-methyl meth- acrylate interpolymer	$1.29 \times 10^{-4}$	$0.98 \times 10^{12}$	-2000
A	Vulcanized Neoprene	$2.08 \times 10^{-4}$	$0.72 \times 10^{12}$	-1630
	Butadiene-styrene inter- polymer	$2.75 \times 10^{-4}$	$0.63 \times 10^{12}$	-1100
	Butadiene-methylmetha- crylate interpolymer	$1.66 \times 10^{-4}$	$0.69 \times 10^{12}$	-1450

$v_0$  was obtained from the solubility constant  $\delta$  at  $p = 1$  atm. and  $T = 300^\circ$  K expressed as cc. at N.T.P. per cc. of rubber, by the relation:

$$v_0 = \frac{\delta \times \text{mol. vol. of solute}}{22,400}$$

Assumed molecular volumes were 26.4, 32.8 and 28.1 cc. for hydrogen, nitrogen and argon, respectively.

so from the limiting slope of the curve of  $v_0$  against  $p/p_s$ ,  $z$  may be found. For benzene in rubber,  $z$  was found in this way to be 3.53 at  $25^\circ$  C and 4.07 at  $100^\circ$  C. Figure 2 (a) gives experimental points for the  $100^\circ$  and  $25^\circ$  isotherms, while the full curves are calculated from Equation (14a), using the values of  $z$  above. Agreement over the whole range of compositions is extremely good.

Less accurate and complete vapor pressure-composition data are available for *n*-heptane<sup>21</sup>, toluene<sup>22</sup>, and chloroform-rubber<sup>23</sup> systems for which  $w$  is also small<sup>21</sup>. Figures 2 (b), 2 (c) and 2 (d) indicate the degree of success obtained with the simple isotherm Equation (14a), and it is seen that values of  $z$  of about 4 (chosen by analogy with the benzene-rubber system) give very reasonable agreement, although small divergencies are noted<sup>25</sup>.

*Comparison with experiment: isotherms of vapors partially miscible with rubber.*—Partial miscibility of a vapor in an elastomer signifies that  $w$  is no longer negligible, so Orr's equation (Equation (4)) must be used to derive the isotherm, giving:

$$\frac{v_0(\beta + 1 - 2x)^{z/2}}{\{ (1 - 2/z \cdot v_r)(\beta + 1)(1 - x) \}^{z/2}} = p/p_s \quad (19)$$

Figure 1 (a), Curves 4, 5, 6 and 7, shows characteristic isotherms obtained using Equation (19), for  $z = 4$  and various values of  $w$ .

Data for testing Equation (19) are seldom complete or very accurate; among the best are those of Lens<sup>26</sup> for the acetone-rubber system. Figure 3 shows experimental isotherm data and also points calculated from Equation (19) with  $z = 4$ ,  $w = 848$  cal., the temperature being  $35^\circ$  C. The isotherm:

$$\ln v_0 + (1 - v_0) + \mu(1 - v_0)^2 = \ln p/p_s \quad (20)$$

based on an approximate equation of Huggins<sup>10</sup> was also examined. With  $\mu = 1.45$  there is agreement for smaller values of  $v_0$  but marked divergence later.

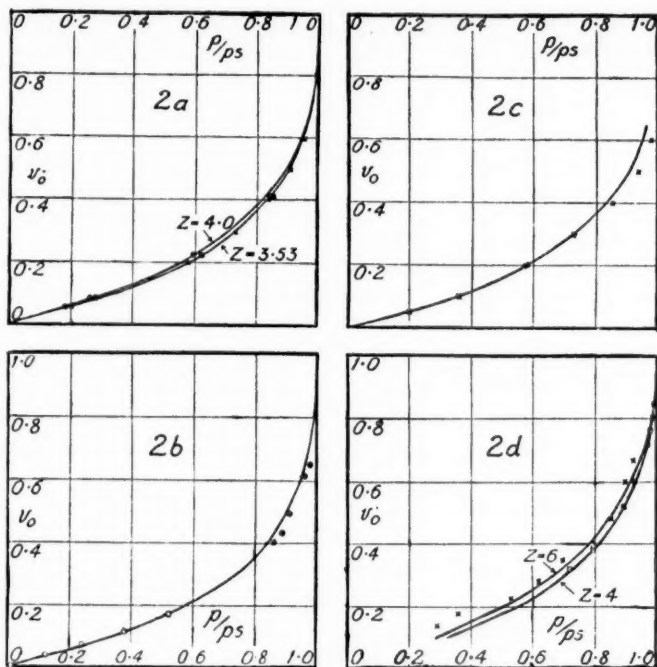


Fig. 2.—The isotherm  $\frac{v_0}{(1 - 2/zv_r)^{1/2}} = p/p_s$  applied to several vapor-rubber equilibria.

- (a) Benzene-rubber<sup>24</sup>:  
 ○ = Experimental data at 100° C } The full curves are calculated isotherms, using  $z = 4.0$  and  $3.53$ .  
 X, □ = Experimental data at 25° C }  
 (b) *n*-Heptane-rubber<sup>18</sup>:  
 ○ = Experimental data at 40° C. The full curve is calculated using  $z = 3.5$ .  
 (c) Toluene-rubber<sup>19</sup>:  
 X = Experimental data at 30° C. The full curve is calculated using  $z = 3.5$ .  
 (d) Chloroform-rubber<sup>16,17</sup>:  
 X = Experimental data at 35° C } The full curves are calculated using  $z = 4$  and  $z = 6$ .  
 □ = Experimental data at 25° C }

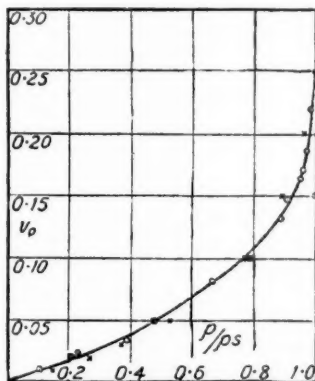


Fig. 3.—Isotherm of acetone in rubber<sup>17</sup>. ○ = Experimental points. X = Calculated from Equation 19 with  $z = 4$ ,  $w = 848$  cal. and  $T = 35^\circ \text{C}$ . □ = Calculated from Equation 20, with  $\mu = 1.45$ .

Orr's equation, however, gives an isotherm which is able to cover the whole composition range reasonably well.

### SUMMARY

A simple extension of the statistics of liquid-elastomer mixtures gives explicitly the sorption isotherm of gases in elastomers at temperatures above their critical temperatures. This isotherm has been used to compare the experimental and theoretical solubility constants of several permanent gases in various elastomers, with good agreement.

Isotherms of a number of vapors in rubbers were also calculated. In the case of the benzene-rubber system the actual data are very successfully reproduced by the isotherm derived from Miller's equation, which assumes random mixing  $\left( \frac{v_0}{(1 - 2/zv_r)^{z/2}} = p/p_s \right)$ . Other mixtures which do not deviate greatly from this isotherm were chloroform-rubber, *n*-heptane-rubber and toluene-rubber.

Orr's equation was moderately successful in giving the isotherm for acetone in rubber, a system in which a larger endothermal heat of mixing of liquid and rubber causes departures from random mixing and results eventually in a two-phase system at a critical composition. An equation of Huggins in this case led to a less satisfactory isotherm.

### REFERENCES

- <sup>1</sup> Fowler and Guggenheim, "Statistical Thermodynamics", C. U. P., 1939, Chap. 10.
- <sup>2</sup> Fowler and Guggenheim, "Statistical Thermodynamics", C. U. P., 1939, p. 554; Lacher, *Proc. Roy. Soc. 161A*, 525 (1937); Barrer, *Trans. Faraday Soc.* **40**, 374 (1944).
- <sup>3</sup> Brunauer, Emmitt and Teller, *J. Am. Chem. Soc.* **60**, 309 (1938); Brunauer, Deming, Deming and Teller, *J. Am. Chem. Soc.* **62**, 1723 (1940); Brunauer, "The Adsorption of Gases and Vapors", O. U. P., 1944, Chap. 6; Foster, *J. Chem. Soc.* 1945; see also Hill, *J. Chem. Physics* **14**, 263 (1946) for statistical derivation.
- <sup>4</sup> Cassie, *Trans. Faraday Soc.* **41**, 450 (1945).
- <sup>5</sup> Orr, private communication.
- <sup>6</sup> Brunauer, Emmitt and Teller, *J. Am. Chem. Soc.* **60**, 309 (1938). Usually called the BET isotherm.
- <sup>7</sup> Brunauer, "The Adsorption of Gases and Vapors", O. U. P., 1944, Figures 73, 74.
- <sup>8</sup> Meyer, *Helv. Chim. Acta* **23**, 1063 (1940).
- <sup>9</sup> Flory, *J. Chem. Physics* **9**, 660 (1941); **10**, 51 (1942).
- <sup>10</sup> Huggins, *J. Chem. Physics* **9**, 440 (1941); *Ann. N. Y. Acad. Sci.* **43**, 1 (1942); *J. Phys. Chem.* **46**, 1 (1942); *J. Am. Chem. Soc.* **64**, 1712 (1942).
- <sup>11</sup> Miller, *Proc. Cambridge Phil. Soc.* **38**, 109 (1942).
- <sup>12</sup> Orr, *Trans. Faraday Soc.* **40**, 320 (1944).
- <sup>13</sup> Scott and Magat, *J. Chem. Physics* **13**, 172 (1945); Scott, *J. Chem. Physics* **13**, 178 (1945).
- <sup>14</sup> Developments of the statistical theory according to a modified lattice model, in which each molecule of solute occupies several sites have, nevertheless, shown some approach to the form of Flory's equation for zero heating of mixing (cf. Guggenheim, *Proc. Roy. Soc.* **183A**, 203 (1944); Miller, *Nature* **157**, 842 (1946); Gee, "Discussion on Swelling and Shrinking", *Trans. Faraday Soc.*, in press).
- <sup>15</sup> Ferry, Gee and Treloar, *Trans. Faraday Soc.* **41**, 340 (1945). However, the relation of *w* and the experimental heat of mixing is not clear. Equations 20b or 25b of Orr (*Trans. Faraday Soc.* **40**, 320 (1944)) give partial molal heats of mixing of a hypothetical condensed phase of pure monomer in which monomer molecules are distributed on the lattice sites of coordination number *z* with a lattice of similarly distributed pure polymer. The relationship that such phases bear, for example, to the actual structure of liquids such as benzene or toluene to be mixed with the rubbers cannot be established with certainty. Moreover *W* of Equation 4c does not include the heat of condensation of vapor to give the hypothetical condensed phase. It seems best, therefore, to use *W* in Orr's equations as a second adjustable constant (in addition to *Z*).
- <sup>16</sup> For zero values of *W*. If *w* is not zero, *χ* is the heat of condensation of 1 mole of gas to give the hypothetical condensed phase referred to in Reference 15.
- <sup>17</sup> Barrer, *Trans. Faraday Soc.* **40**, 374 (1944).
- <sup>18</sup> Barrer, *Trans. Faraday Soc.* **45**, 628 (1939).
- <sup>19</sup> There must be complete miscibility of vapor and elastomer, which precludes many of the data of Stamberger (*J. Chem. Soc.* **1929**, p. 2318) and Lens (*Rec. trav. chim.* **51**, 971 (1932)). Complete miscibility is found when solute and elastomer are of nearly equal polarity, e.g., hydrocarbon-rubber systems.
- <sup>20</sup> Gee and Treloar, *Trans. Faraday Soc.* **38**, 147 (1942); Gee and Orr, *Trans. Faraday Soc.*, in press. The experimental sorption heat (see References 14 and 15) of liquid benzene in rubber is extremely small, so *w* is also likely to be negligible. This is the condition for applicability of Equation 14a (see References 15 and 16).
- <sup>21</sup> Ferry, Gee and Treloar, *Trans. Faraday Soc.* **41**, 340 (1945).
- <sup>22</sup> Meyer, Wolf and Boissonas, *Helv. Chim. Acta* **23**, 430 (1940).
- <sup>23</sup> Stamberger, *J. Chem. Soc.* **1929**, p. 2318; Lens, *Rec. trav. chim.* **51**, 971 (1932).
- <sup>24</sup> Gee and Treloar, *Trans. Faraday Soc.* **38**, 147 (1942); Gee and Orr, *Trans. Faraday Soc.*, in press.
- <sup>25</sup> The direction of these divergences is compatible with small positive values of *w* for the hydrocarbons and with a small negative value for chloroform.
- <sup>26</sup> Lens, *Rec. trav. chim.* **51**, 971 (1932).



# A RADIOGRAPHIC STUDY OF RUBBER-SULFUR MIXTURES \*

J. J. TRILLAT

FACULTY OF SCIENCES, UNIVERSITY OF BESANCON, FRANCE

## INTRODUCTION

It is generally recognized that the size of the grains of sulfur in a rubber mixture and their state of dispersion in the mixture play an important part in the vulcanization process. In a general way this is true also of the dispersion of fillers in industrial rubber mixtures, the variety of which is great and the properties of which depend to a large extent on the nature of the compounding ingredients, on the uniformity of their dispersion, and on their particle size.

The problem, which is so important to the rubber industry, has been studied by numerous methods which need not be discussed at this time. Based on the specific absorptive properties for x-rays, an absorption which increases in proportion to the cube of the atomic number for any given wave length, the attempt has been made in the work described in the present paper to develop a simple method with which it would be possible to follow and to control the incorporation of compounding ingredients in rubber. It should be mentioned incidentally that rubber is composed wholly of light atoms (carbon and hydrogen) and has very little absorptive power for materials which are incorporated into it as fillers, with the exception of carbon black, which is itself a light element.

Before attacking the problem in all its ramifications, it seemed advisable to begin with the simplest case, that of mixtures of rubber and sulfur alone. Sulfur, with atomic number 16, is actually much more absorptive than the hydrocarbon of rubber; accordingly it is possible, with certain precautions, to detect the presence of this in thin sheets of uniform thickness.

It will be realized that the use of ordinary radiography with high tension is impracticable in this case, for the high penetrative power of x-rays would make it impossible to obtain sufficient contrast between rubber and sulfur. It is, in fact, necessary to start with sheets which are sufficiently thin so that there is no excessive superposing of the sulfur grains on the radiograph. For the same reason it is of advantage to use x-rays of relatively great wave length so as to obtain good definition. In addition, the film obtained from any given sample should be enlarged about 15 to 20 times; hence it is necessary to use a fine-grain emulsion which will not mask the phenomenon to be observed after enlargement.

## EXPERIMENTAL METHOD

The points brought out in the discussion above led to the choice of the so-called semimicroradiographic or microradiographic method, which has been used many times so successfully by the present author<sup>1</sup>. From a practical viewpoint, semiradiography is sufficient in itself to obtain satisfactory results.

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 22, No. 3, pages 63-66, March 1945.

The sample of rubber mixture should be of uniform thickness and not have thick spots or irregularities such as wrinkles, hollows or pits, which would result in variable absorption and local excess concentrations of sulfur to be radiographed. To avoid this condition, recourse may be had to either of two techniques: (1) to calender sheets to uniform thickness, which is difficult to accomplish when very thin sheets are desired, or preferably (2) to place the sample between two sheets of cellophane about 0.06 mm. thick and to press the sandwich at 50–60° C in such a way as to squeeze the rubber mixture out flat and at the same time to bond it well to the cellophane. In this second technique, air bubbles difficult to eliminate may remain, but these are easily recognizable and do not in any way lead to misinterpretation of the radiographs.

The thickness of the rubber sheets should in general be of the order of several tenths of a millimeter. In practice, the present author has used samples having a total thickness of 0.18 mm., *i.e.*, a film of rubber 0.12 mm. thick.

The plied sheet samples are placed in an ordinary photographic plate holder, in direct contact with a fine-grained photographic film, *e.g.*, Pathéfilm. The assembly is then exposed to x-rays from a dismantlable tube having a sharp focus (obtained by electrostatic concentration), equipped with a copper anticathode ( $\lambda K_{\alpha} = 1.54 \text{ \AA.U.}$ ), and functioning at a voltage of only 8 kilovolts, with a current of 15–20 milliamperes. Under these conditions, the limiting continuous depth corresponds to a wave length  $\lambda$  of 1.55  $\text{\AA.U.}$ , and a maximum spectrum intensity of approximately 2  $\text{\AA.U.}$  Since the  $K_{\alpha}$  radiation of the copper is 1.54  $\text{\AA.U.}$ , it is not excited, and only softer radiations, localized in the neighborhood of 2  $\text{\AA.U.}$ , are active. The focal distance is 30 cm., under which conditions the time of exposure does not exceed two minutes. The negatives obtained are enlarged 16 times. The experiments which are the subject of the present paper were carried out with samples prepared from vulcanizates<sup>2</sup> containing 1.5, 10, and 32 per cent, respectively, of sulfur.

## EXPERIMENTAL RESULTS

### UNVULCANIZED MIXTURES

Whereas rubber itself, to which no sulfur has been added, gives, as would be expected, a radiograph of uniform color, mixtures of rubber and sulfur give radiographs on which the sulfur appears in the form of black grains standing out clearly on the gray background of the rubber phase. Any air bubbles which may be present appear, on the contrary, as light spots, and cannot be mistaken for sulfur.

Figures 1, 2, and 3 represent calendered sheets of rubber containing 5, 10 and 32 per cent, respectively, of sulfur, and showing slight irregularities in thickness resulting from their preparation.

Figure 1 shows numerous black spots of unequal dimensions, distributed in a fairly regular fashion. It is evident that at the abnormally thick spots, which appear as somewhat darker areas, the distribution of the sulfur grains is more concentrated, as would be expected, since more sulfur grains are encountered by the x-rays in the thicker sections.

Figure 2, which represents a rubber mixture containing 10 per cent of sulfur, is similar to Figure 1, except that the grains of sulfur are more closely distributed, and the proportion of relatively fine grains is much greater than in Figure 1.

Figure 3, which represents a rubber mixture containing 32 per cent of sulfur, shows a still denser distribution of sulfur grains, with a predominance of fine

grains. However, it should be emphasized that it would be wrong to compare Figures 1, 2 and 3 on the basis of their sulfur contents, because of the inevitable differences in thickness between such calendered samples.

On the other hand, with radiographs obtained from samples of the same thickness, prepared with cellophane by the method already described, it is possible to make much more accurate observations, as will be seen by an examination of Figures 4, 5, 6, and 7, which give no indication of the irregular crinkled appearance of the samples shown in Figures 1, 2 and 3.

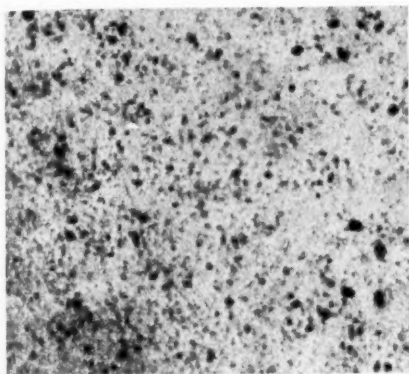


FIG. 1

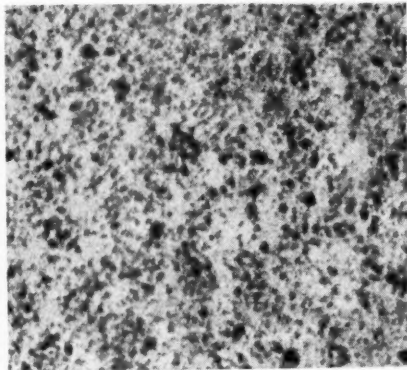


FIG. 2

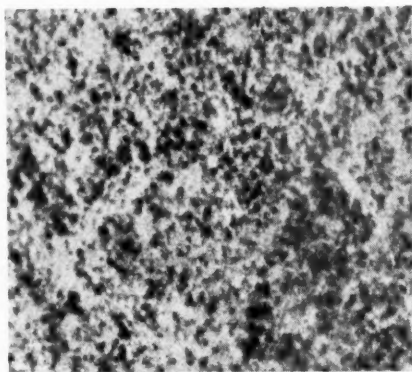


FIG. 3

Unvulcanized rubber mixtures containing 5, 10, and 32 per cent, respectively, of sulfur, and calendered.

Figure 4 represents a thin sheet of rubber, containing 1 per cent of sulfur, and 0.12 mm. thick, prepared by compression between two films of cellophane. Since the cellophane was perfectly uniform and transparent to x-rays, it is not visible in the radiograph any more than is the rubber phase itself. The only things visible are grains of sulfur in the form of black spots, which in this case are too few to be at all prominent.

On the contrary, with increase in the sulfur content, for example, with 5 per cent of sulfur (see Figure 5), the sulfur becomes clearly visible, and stands

out prominently on the gray background of the radiograph. It is evident that the distribution is not very uniform, and that, in addition to lighter very fine grains, there are relatively large grains or aggregates. The size of the sulfur grains lies, as estimated from the radiograph, between about 0.025 mm. and 0.125 mm. It should be easy, knowing the magnification ( $\times 16$ ), to calculate the number of grains per unit surface area, and thereby to measure the uniformity of distribution as well as the distribution curve as a function of the size of the grains.

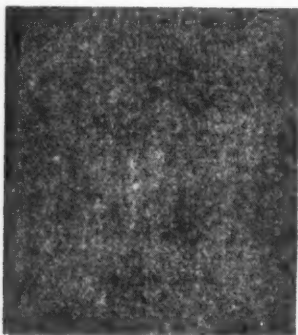


FIG. 4

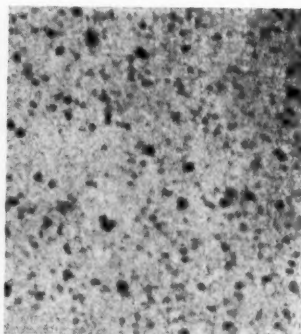


FIG. 5

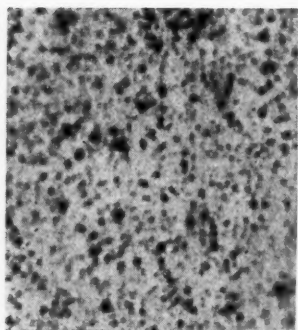


FIG. 6

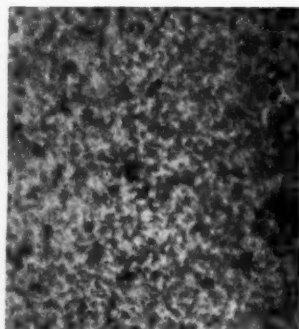


FIG. 7

Unvulcanized rubber mixtures containing 1, 5, 10, and 32 per cent, respectively, of sulfur, and pressed out with cellophane.

Figure 6 represents a mixture containing 10 per cent of sulfur. Here the grains are much more closely distributed, but it is still possible to count the distribution. Here too large grains are visible among the smaller grains. The size of the grains lies within the range of 0.03 mm. and 0.125 mm.

Figure 7 represents an ebonite mixture containing a much higher proportion of sulfur, *viz.*, 32 per cent. Here the number of grains per square centimeter is very large, and the distribution appears to be uniform, with a much more nearly uniform size of grain of the order of 0.03–0.05 mm. Some relatively large grains persist, however. It is certain that this limitation in the size of grain within a very narrow range or average dimension is attributable to the fact that a relatively long time was required to incorporate all of the sulfur into the rubber on a mixing mill.

Finally these experiments show that sulfur present in mixtures of rubber and sulfur is easily visible by radiography. With pictures obtained by this method it is possible to study the conditions of mixing sulfur, and perhaps in the same way fillers, into rubber as a function of the time of mixing, temperature, etc. It is possible also to determine statistically the size of the sulfur grains and the uniformity of their distribution per unit volume.

#### VULCANIZED MIXTURES

It is known that, during vulcanization, part of the free sulfur present combines with the rubber, with formation of bridges between the macromolecules of hydrocarbon, and thereby imparts to the rubber remarkable elastic properties. In view of this it seemed of particular interest to examine, after vulcanization the samples which had already been examined before they had been vulcanized to ascertain how free sulfur remaining after vulcanization and the combined sulfur are distributed and in what physical state they are presented in vulcanized rubber.

In this study samples prepared by light compression between two sheets of cellophane were used. In the first series, samples containing from 1 to 32 per cent of sulfur were vulcanized for 6 hours at  $143^{\circ}\text{C}$ ; in a second series, a sample containing 32 per cent of sulfur was vulcanized for different lengths of time at  $143^{\circ}\text{C}$ .

*First series. Influence of the sulfur content.*—The radiographs were prepared by the same technique and under the same experimental conditions as in the experiments already described (8 kilovolts). The samples contained 1, 5, 10 and 32 per cent, respectively, of sulfur and were all vulcanized for 6 hours at  $143^{\circ}\text{C}$ .

An essential difference is at once evident between these radiographs and those obtained from the same samples before vulcanization. Whereas before vulcanization the sulfur appears in very sharply defined form, it is, after vulcanization, no longer distinguishable. All the radiographs showed a uniform gray color, on which as a background no spots due to sulfur grains were visible. For this reason only the radiograph of the mixture containing 32 per cent of sulfur is shown (see Figure 8).

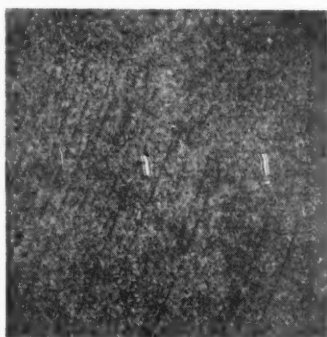


FIG. 8.—Rubber-sulfur mixture containing 32 per cent of sulfur, vulcanized 6 hours at  $143^{\circ}\text{C}$ .

Consequently vulcanization, at least under the conditions described above, is characterized by the disappearance of sulfur in granular form, and the dispersion of the sulfur uniformly throughout the elastic mass.



Now it is known that the greater part of the sulfur combines with the rubber hydrocarbon and that the remaining sulfur, designated as free or uncombined sulfur, is extractable with various solvents such as acetone. The proportion of combined sulfur increases rapidly with the time of vulcanization to a point where only a very small proportion of sulfur remains in the free state. Under some conditions the combination of sulfur with rubber may be substantially complete after a sufficiently long time of vulcanization. This combined sulfur is not visible in radiographs, since it is dispersed in a statistically uniform way, no longer in the form of grains, but as atoms functioning as bridges between the macromolecules of the hydrocarbon.

Furthermore, the remaining free sulfur is fused at the temperature of vulcanization (in this case  $143^{\circ}\text{C}$ ) and, after cooling, it is possible that it remains in solution in the rubber, from which it can, unlike the combined sulfur, be extracted by suitable solvents. The tests which have been described do not make it possible to say whether any free sulfur was still present in this state in the vulcanized samples. The tests indicate only that, for some reason, grains of sulfur can no longer be detected by radiography, at least with the magnification used in the present work.

*Second series. Influence of the time of vulcanization.*—These tests were carried out with a rubber-sulfur mixture containing 32 per cent of sulfur, vulcanized at  $143^{\circ}\text{C}$  for 15 minutes, 30 minutes, 1 hour, 3 hours, and 6 hours, respectively. Under these conditions it was hoped to follow the progressive combination of sulfur and the corresponding progressive disappearance of sulfur grains.

The results were very satisfactory. Consider the unvulcanized mixture containing 32 per cent of sulfur, the radiograph of which is shown in Figure 7. After vulcanization for 15 minutes at  $143^{\circ}\text{C}$ , it gave the radiograph shown in Figure 9, which is particularly interesting when compared with Figure 7.

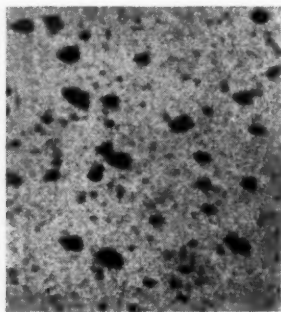


FIG. 9

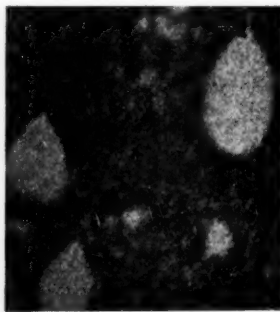


FIG. 10

Rubber-sulfur mixture containing 32 per cent of sulfur, heated 15 minutes at  $143^{\circ}\text{C}$ .

It is evident, for example, that a large part of the sulfur has disappeared and that only a few small grains remain. The greater part of the uncombined sulfur is agglomerated into large flat drops having an elliptical form, and still visible in Figure 10 obtained with a magnification of 100. Here the sulfur appears white. The formation of these droplets is easily explained by the fact that, at the temperature of vulcanization, *viz.*,  $143^{\circ}\text{C}$ , the sulfur is fused.

After vulcanization for 30 minutes at  $143^{\circ}\text{C}$ , the number of sulfur grains



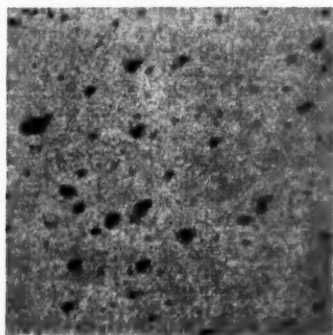


FIG. 11.—Rubber-sulfur mixture containing 32 per cent of sulfur, heated 30 minutes at 143° C.

has decreased still more (see Figure 11), but large droplets persist, together with a certain number of fine grains.

After vulcanization for 1 hour or longer, the radiographs no longer showed any trace of sulfur, and the pictures obtained were all identical to that shown in Figure 8. Accordingly all free sulfur disappeared, as far as was manifest by radiography, sometime between 30 minutes and 1 hour of vulcanization. It is impossible, however, to say whether or not some sulfur might still have been in solution, for, if so, it would not be detected nor otherwise distinguished from combined sulfur.

So as not to be confused by grains of the Pathélit emulsion, which appear to a certain extent on magnification, the tests were repeated with the use of a film, specially prepared for microradiography and having an extremely small size of grain (Lippmann Kodak film). This was much less rapid than the film used before, but it gave a greater fineness of detail. In addition, a new sealed tube (Philips) was used. This was constructed specially to have an extremely sharp focus (0.3 mm.) and to give very sharp radiographs. With 10 kilovolts, a consumption of 1.4 milliamperes, and a focal distance of 5 cm., the time of exposure was 4 minutes.

Under these conditions it was found that the samples containing 32 per cent of sulfur and which had been vulcanized for 15 minutes and for 30 minutes at

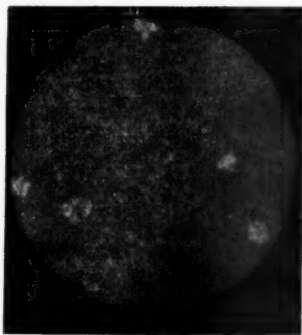


FIG. 12.—Rubber-sulfur mixture containing 32 per cent of sulfur, vulcanized 1 hour at 143° C. Visible efflorescence of sulfur.

143° C showed the same phenomena already described, *i.e.*, droplets of sulfur (see Figures 9, 10 and 11). On the other hand, a sample vulcanized for 1 hour showed a very characteristic efflorescence of sulfur (at a magnification of 31 (see Figure 12)), and no droplets of sulfur were visible. This phenomenon was manifest also, although to a lesser degree, after vulcanization for 3 hours, but it disappeared completely after vulcanization for 6 hours; hence the entire radiograph has a uniform gray hue. This efflorescence of sulfur is unquestionably attributable to free sulfur, which after vulcanization migrates out of the rubber and recrystallizes after a certain time. It might be questioned why the free sulfur in droplets does not exhibit this peculiar appearance. This merits special study, for it is probable that certain peculiar physical conditions influence the susceptibility of the sulfur to recrystallize as an efflorescence.

In any event, it is possible that, under other conditions of vulcanization, notably with accelerators present, with which vulcanization can be carried out below the melting point of sulfur, the latter will remain in granular form, and can be detected by radiography, with x-rays of relatively long wave length.

### CONCLUSIONS

The method described in the present paper suggests certain interesting applications in the rubber industry, important among which are:

- (1) the study of the mixing of sulfur and of fillers into rubber as a function of the time of milling, temperature, etc.;
- (2) the study of the uniformity of distribution of sulfur grains and of fillers;
- (3) the statistical determination of the size of grains;
- (4) the study of vulcanization, particularly the proportions of free sulfur and combined sulfur after vulcanization, the influence of accelerators, and the size of sulfur grains as affected by vulcanization.

It should be realized that in the present paper only the principles of the radiographic method have been outlined, and it remains for those in the industry who have problems of the kind to apply the method to the particular problems which arise and may be solved by this method. Excellent results have been obtained by the present author in an investigation of a similar kind, involving the grinding and dispersion of pigments in paints and varnishes<sup>3</sup>.

### ACKNOWLEDGMENT

The work described in the present paper was carried out in the x-ray and electronic optics laboratories of the National Center of Scientific Research, in collaboration with the French Rubber Institute, which was kind enough to prepare the samples for the work and to discuss with the author the results of the work.

### REFERENCES

- <sup>1</sup> Trillat, *Rev. scientifique* 1940, No. 4, pp. 212; *Compt. rend.* 213, 833 (1941); 214, 164 (1942); 216, 179, 534, 683 (1943); *Sci. ind. photo.* 12, 1 (1942); *Bull. soc. franc. electriciens* 3, 25 (1943); "Pigments, peintures, et Vernis", in press; Paic, *Compt. rend.* 213, 572 (1941).
- <sup>2</sup> These vulcanizates were prepared and furnished by the French Rubber Institute.
- <sup>3</sup> Trillat, "Pigments, Peintures, et Vernis", in press.

# PLASTICIZATION OF NATURAL AND SYNTHETIC RUBBERS. I\*

G. H. PIPER AND J. R. SCOTT

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

## SUMMARY

This report describes the first part of an investigation on the factors operative in the plasticization of natural and synthetic rubbers, with special reference to determining the exact part which each one plays and to elucidating the changes in molecular structure which are the fundamental causes of the effects produced. The main conclusions from the work so far completed are as follows.

## NATURAL RUBBER

(1) Natural rubber can be plasticized to a greater or less extent by any one of the following methods: heat, oxidation, mechanical working, absorption of a softener (oil). The heat involved in ordinary milling, however, is insufficient to have any plasticizing effect, and the same is true of oxidation unless this is activated by the mechanical strain to which the rubber molecules are subjected during milling. The effectiveness of milling appears, therefore, to be due largely to mechanical breakage and straining of the rubber molecules. In high-temperature breakdown in an internal mixer, mechanical action is probably aided more by thermal breakdown, because the temperatures used ( $160^{\circ}$ – $200^{\circ}$  C) are sufficient in themselves to produce some plasticization.

(2) The effects of heat, oxidation, mechanical working, and absorbed softener on plastic properties are quite different, so that it is not immaterial which of these factors is used in plasticizing rubber. In particular, subjection to temperatures between about  $150^{\circ}$  and  $250^{\circ}$  C increases nerve, as shown, for instance, by higher elastic recovery. Mechanical working is the most effective means of reducing nerve, which is an important aim in plasticizing rubber; an oil softener also helps in this direction.

(3) Plasticization by heat alone appears to require a temperature of about  $260^{\circ}$  C to give a product similar to ordinary masticated rubber. Temperature control is critical, however, because  $250^{\circ}$  C is not effective, and  $275^{\circ}$  C simply melts the rubber. Theoretically a heat treatment is more economical than mastication, as the latter needs about eight times as much energy as is needed to heat rubber to  $260^{\circ}$  C, and all this energy is ultimately lost.

(4) Oxidative softening is practicable only at quite high temperatures, unless an oxidation catalyst can be introduced into the rubber, since the rate of uncatalyzed oxidation at, say,  $70^{\circ}$  C is far too slow even with a high pressure of oxygen.

(5) Consideration of the mechanism of rubber processing operations—mixing, calendering, extrusion, adhesion, open-steam vulcanization—shows that their success depends on having rubber with the correct plastic properties<sup>1</sup>.

\* Reprinted from the *Journal of Rubber Research*, Vol. 16, No. 6, pages 151–160, June 1947.

The present results show that these properties depend on whether heat, oxidation, mechanical working, or addition of softener has predominated in the plasticizing treatment, whence it appears that closer control of processing characteristics could be secured by correct choice of the plasticizing factors, a subject which merits a much fuller study.

#### SYNTHETIC RUBBERS

(1) Comparison of the plastic properties of milled natural and butadiene-styrene (GR-S) rubbers helps to explain certain processing difficulties met with the latter, notably the unsatisfactory tackiness or self-adhesion. This can be attributed, in part at least, to the fact that the synthetic rubber, even after milling, does not flow readily under very small stresses, as does natural rubber. This may be due to its having to some extent a network structure with cross-links between the molecular chains, or alternatively, to the chains having a molecular structure favorable to chain entanglement.

(2) Butadiene-styrene and butadiene-acrylonitrile copolymers cannot be plasticized by heat alone; in this respect they differ from natural rubber, which shows a definite softening when heated in absence of air at 200° C or above.

(3) In processing these types of synthetic rubber, application of heat in absence of oxygen or mechanical working should be avoided, because it produces an effect similar to scorching, and which is tentatively ascribed to cross-linking of the chain-molecules.

(4) In plasticizing GR-S by heating in air or oxygen, it is important to ensure that oxygen penetrates throughout the rubber, because any parts not reached by the oxygen will, in effect, become scorched instead of plasticized. Factors favoring uniform oxygen penetration are avoidance of unduly high temperatures or thick masses of rubber, and use of increased oxygen pressures.

(5) The success of cold milling for plasticizing GR-S is in agreement with the present results, which also show that bad results are obtained in plasticizing GR-S in an internal mixer if the temperature is allowed to become too high, and particularly if the freshly worked material is allowed to remain very hot after removal from the mixer.

(6) As the tendency of GR-S to harden, at high temperatures, seems to persist after vulcanization, it is unlikely that high-temperature (thermal) reclaiming processes will be successful for GR-S unless some means for preventing cross-linking can be found.

#### (1) INTRODUCTION

The object of this investigation on the plasticization of unvulcanized rubbers, of which the first part is described here, is to study the factors responsible for the plasticizing effect and, in particular, to discover the exact part which each one individually plays. It is hoped to study both the changes in plastic or flow properties, which are extremely important as determining the behavior of the plasticized rubber in processing operations, and also the changes in molecular structure on which the plastic properties depend. It is hoped in this way first to gain an insight into the fundamental mechanism of plasticization and, secondly, to enable plasticization to be carried out more economically, and processing behavior to be controlled more effectively than at present, by correct choice of plasticizing agencies and conditions.

It was originally intended to defer the commencement of this research pending the development of a plastometer by which the fundamental plastic

properties, namely, the flow curve, or relation between shearing stress and rate of shear, and the extent and rate of recovery, could be studied satisfactorily. As it became evident that the completion of this instrument (the shearing-cone plastometer, described by Scott<sup>1</sup>) would take a considerable time, it was decided to make a preliminary survey of the effects of certain plasticizing factors—heat, oxidation, mechanical working, and absorption of a softener (mineral oil)—using the parallel-plate plastometer to examine plastic properties. The present report describes this preliminary work. Most of this has been carried out with the natural rubber, but some observations on Buna-S and GR-S are included; a later report will describe a fuller study of GR-S.

In previous work on the part played by various factors in plasticizing treatments, the resultant effects have been measured in terms of the conventional plasticity figures or of solution viscosity, and hence give little or no information on the fundamental flow properties, which it is the object of the present research to elucidate.

Porritt and Fry<sup>2</sup> investigated the effect on the benzene solution viscosities of heating rubber at 150° C *in vacuo* and in oxygen. They found that heating in air produced a decrease in viscosity, depending on the amount of oxygen present. They concluded that raw rubber may be heated at 150° C *in vacuo* without any marked effect on its solution viscosity, provided all traces of oxygen were removed. Examination of their results shows, however, a slight decrease in the solution viscosity. Staudinger and Geiger<sup>3</sup> carried out similar experiments, and detected some softening on heating *in vacuo*. Grenquist<sup>4</sup> investigated the effect of heating in air, oxygen, steam, and carbon dioxide. The plasticity increased in all four cases, and at 70° C the softening proceeded at almost the same rate whether heating was in air or in relatively inert carbon dioxide. Farberov and Margolina<sup>5</sup> heated rubber at 130°–170° C in oxygen and in inert gases; with the latter only slight softening was observed, whereas with oxygen there was a relation between the plasticizing effect and the oxygen concentration. When heating *in vacuo* the higher the vacuum (their highest vacuum was 35 mm.) the less was the plasticization.

Since the present investigation was undertaken, Bolland and Orr<sup>28</sup> have shown that heat in the absence of oxygen can cause degradation of the rubber molecule.

The effect of mastication and the part played by oxygen in this process have been studied in some detail, owing to the great technical interest involved. Fry and Porritt<sup>2</sup> suggested that the effect of milling was due to oxidation. Cotton<sup>6</sup> masticated rubber in an internal mixer in various gases and concluded that the oxygen present during mastication of raw rubber is responsible for the increase in plasticity which occurs. In presence of oxygen rubber gained slightly in weight and this was attributed to oxidation. Staudinger<sup>7</sup> showed that there was a decrease in molecular weight of the rubber during mastication. Busse<sup>8</sup> concluded that softening on the mill is due to the breaking up of the long rubber molecules into shorter ones by oxidation. In further work Busse and Cunningham<sup>9</sup> found that appreciable plasticization was produced by masticating in an atmosphere of nitrogen, but the effect was not so large as in air. The subject is discussed more fully by Gallay<sup>10</sup>.

Previous work carried out on synthetic rubbers is referred to in Section 4.

The general conclusion from published data is, therefore, that natural rubber can be plasticized to some extent by mechanical working alone, but that in ordinary mastication oxidation plays an important—possibly a predominant—part. Evidence regarding the plasticizing effect of heat in the absence of these



other factors is conflicting, but on the whole indicates the absence of any pronounced effect at normal milling temperatures. No information is available to show whether the individual plasticizing factors, such as oxidation, mechanical working, and addition of softener, produce identical changes in the plastic properties of the rubber.

## (2) EXPERIMENTAL METHODS

### (2.1) RUBBERS USED

The natural rubbers used were: (1) smoked sheet; (2) smoked sheet, acetone-extracted (effect of heat only); (3) purified rubber, from centrifuged latex (effect of heat only).

The latex rubber was prepared with the object of obtaining a rubber hydrocarbon free from resinous materials, oxidized rubber, and oxygen-containing impurities,<sup>11,12,13</sup> which might influence its reaction towards plasticizing treatments. The latex was centrifuged repeatedly and, after drying in the absence of oxygen, the rubber was acetone-extracted in the dark for 5.5 hours.

The synthetic rubbers used were: (1) butadiene-styrene copolymers: Buna-S (German) and GR-S (American); (2) butadiene-acrylonitrile copolymer (Hycar-OR); (3) Neoprene-E; (4) Thiokol-F. These were not subjected to any purification treatment before being used.

### (2.2) TREATMENTS

*Heat in the absence of oxygen.*—The plasticity measurements were made with 1-cc. cylindrical pellets (except for Hycar-OR, where cubes of 1.3 cm. side were used) and the rubbers were heated in this form.

The pellets of smoked sheet were made by grinding off the corrugations on the smoked sheet and rolling up strips into cylindrical form, later trimming to a height 10.8 mm. and weight 0.92 gm. The Buna-S was in the form of crumb and the pellets were made by consolidating the hot crumb in a cylindrical mould kept at 100° C.

The pellets were heated in a glass vessel connected via a vapor trap with a Töpler pump for obtaining a high vacuum, the whole constituting an all-glass sealed system. Great care was taken to remove all traces of oxygen; a prolonged out-gassing treatment was given before heating, to remove absorbed or entrapped air. The period of heating was 2 hours, except where otherwise stated.

*Oxidation.*—Strips of smoked sheet with the corrugations ground off were placed in an oxygen bomb and subjected to 60 lbs. per sq. in. oxygen pressure at 70° C for periods of 1, 2, and 7 days. The strips were then rolled into cylindrical form for plasticity measurements.

*Milling (cold mastication).*—It was desired to investigate the effect of milling on the plastic flow properties of rubber, under conditions which would minimize or exclude any simultaneous plasticization resulting from oxidation or heat. Two series of tests were carried out:

(1) Smoked sheet was milled on cold rolls with a friction ratio of 3:2 and constant nip of  $\frac{3}{16}$  inch. The rubber was not allowed to form a sheet around the front roll, and sufficient time was given between separate passes to avoid any but a slight rise in temperature in the bulk of the material.

(2) As above, but the rubber contained 2 per cent of hydroquinone incorporated by soaking the rubber in an ethereal solution and drying. This



antioxidant was selected after consideration of the results of Blake and Bruce<sup>14</sup> who found some antioxidants for vulcanized rubber actually accelerated the development of tackiness and rate of oxidation of raw rubber in ultraviolet light. Hydroquinone is a true antioxidant for raw rubber.

*Absorption of softener.*—Smoked sheet with the corrugations buffed off was immersed for short periods in a hydrocarbon (spindle) oil, drained, and weighed. The swollen rubber was then kept at 40° C for 1.5 hours to distribute the oil evenly, and then rolled into cylindrical pellets.

### (2.3) MEASUREMENT OF PLASTIC PROPERTIES

*Plasticity.*—This was measured by the parallel-plate plastometer at 90° C. This instrument does not give the rate of plastic shear of the material at a given stress directly, but measurements can be used to calculate the fundamental plasticity constants of the material indirectly by the method developed by Scott<sup>15</sup> applicable to materials which obey the law of plastic flow:

$$\text{Rate of shear} = \left( \frac{F - f}{c} \right)^n \quad (1)$$

where  $F$  is the shearing stress;  
 $f$  is the friction or yield value of the material;  
 $c$  is the consistency of the material (reciprocal of fluidity);  
 $n$  is a positive numerical constant.

For many materials the yield value is zero and  $n$  is unity, i.e.:

$$\text{Rate of shear} = \frac{F}{c}$$

a type of flow designated true viscous flow. In other cases  $n$  is greater than unity and the flow-stress curve is convex to the stress axis (quasi-flow).

In practice, readings of the thickness in the plastometer were made at short intervals up to 30 minutes compression, the 5-kg. load raised, and the pellet allowed to recover for 24 hours at 90° C, after which its thickness was again measured. The results were analyzed, and it was usually found that the above law of plastic flow was obeyed over the range of shear rates studied; in these cases  $f$  was negligible (except for Thiokol-F).

In tables 1 and 2:

$y_5$  and  $y_{30}$  are the thicknesses (mm.) of the pellet at 5 and 30 minutes compression, respectively, in the plastometer.

Percentage recovery is the recovery ( $y_R - y_{30}$ ) expressed as a percentage of ( $y_0 - y_{30}$ ), where  $y_0$  is the initial thickness of the pellet (10.8 mm.) and  $y_R$  is the thickness after recovery.

$n$  is the index appearing in Equation (1) above.

*Recovery.*—Although the recovery was measured as above, the method is not ideal, since it measures the recovery after compression for a fixed time, and thus a more plastic stock is compressed to a smaller thickness. The recovery after compression to a fixed thickness in a given time would be a more valuable figure, and further, this figure is the one concerned in works practice, as in extruding and calendering. The above recovery figure gives, however, approximately relative values sufficient to show big changes in this property.

TABLE 1

Rubber	Treatment	$\eta_{sp}$	$\eta_{sp}$	Percent- age re- covery	n	Molec- ular weight
Smoked sheet	Nil	3.49	2.85	24.5	3.0	335,000
	Heated 150° C for 2 hours	3.40	2.87	—	3.4	320,000
	200° C for 2 hours	3.11	2.71	68	4.5	290,000
	250° C for 2 hours	1.62	1.25	12	2.7	—
Smoked sheet	Nil	3.87	3.19	30	3.3	—
	Acetone-extracted	5.13	4.13	60	2.9	—
	Acetone-extracted and heated 200° C	3.72	3.18	72	3.37	—
Smoked sheet	Nil	3.93	3.20	46	2.8	340,000
	Oxidized 1 day	3.73	3.04	62	2.9	360,000
	2 days	3.68	2.96	73	2.8	350,000
	7 days	2.78	1.98	50	1.8	200,000
Smoked sheet	Nil	3.82	3.04	24	2.5	405,000
	Masticated 5 minutes	2.71	2.07	3.8	2.0	250,000
	10 minutes	2.35	1.77	1.7	1.8	220,000
	20 minutes	2.00	1.5	0	1.67	175,000
	40 minutes	1.60	1.2	0	1.64	—
	60 minutes	1.36	1.0	0	1.64	140,000
	(Hot mastication, 1000 g.)					
Smoked sheet	Nil	4.07	3.22	27	2.8	—
	Cold masticated 15 passes	3.58	2.96	15	2.9	—
	30 passes	3.68	3.0	12.6	2.9	—
	70 passes	3.25	2.66	10	2.9	—
	150 passes	2.74	—	—	2.6	—
	(200 g. batch)					
Smoked sheet +2% hydro- quinone	Cold masticated 10 passes	3.37	2.84	12	3.3	—
	25 passes	3.51	2.82	11	2.7	—
	40 passes	3.11	2.70	4	3.2	—
	90 passes	3.00	2.47	4	3.3	—
	200 passes	2.46	—	—	2.6	—
Smoked sheet	Nil	3.98	3.20	38.7	2.8	—
	+6.1% oil	3.55	2.91	35.2	2.8	—
	10.4% oil	3.40	2.76	—	2.8	—
	12.5% oil	3.20	2.59	—	2.56	—
	19.96% oil	2.91	2.29	21.3	1.8-2.5	—

TABLE 2

Rubber	Treatment	$\eta_{sp}$	$\eta_{sp}$	Percent- age re- covery	n
Buna-S (German)	Nil	4.08	3.66	77	6.1
	Heated 200° C for 70 minutes	6.70	6.18	96	7.4
	Heated 330° C for 2.75 hours	*			
	Heated in air and masticated	2.03	1.59	2	2.4
GR-S	Nil	2.56	2.18	16.5	3.9
	Heated 150° C for 4 hours	2.87	2.50	78	4.6
	Cold masticated 20 mins. (200 gm.)	1.99	1.65	2.9	3.0
	Cold masticated with iron naphthenate	1.34	1.11	0.9	3
	Nil (another batch)	2.62	2.29	13.4	4.6
	Warm masticated 20 mins. (200 gm.)	2.32	2.00	3	4.3
Hycar-OR	Nil	4.95	4.32	58	—
	Heated 200° C for 70 minutes	9.68	9.52	95	—
	Heated 330° C for 2.75 hours	*			

\* Hard solid, hence impossible to carry out plasticity tests.

## (2.4) MOLECULAR WEIGHT

The average molecular weights of some of the rubbers were determined from the viscosities of the benzene solutions. Acknowledgment is made of their assistance in carrying out these determinations.

## (3) RESULTS FOR NATURAL RUBBER

The results for the various plasticizing treatments are given in Table 1 and are summarized below. Results for smoked sheet masticated for various periods on hot rolls in the normal manner are included for comparison. The effects are shown graphically in Figures 1 and 2.

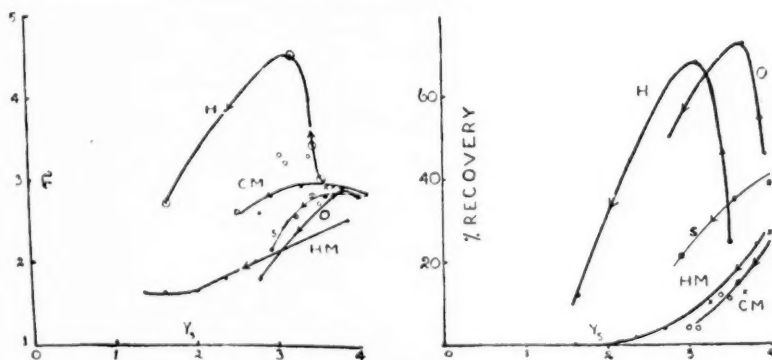


Fig. 1.—Effect of various treatments on plastic properties

H = heating; O = oxidation; CM = cold mastication (x = alone, o = hydroquinone); HM = hot (normal) mastication; S = softener (oil). Arrows show the direction of increasing severity of treatment, i.e., higher temperature of heating, or longer period of oxidation or mastication, or increasing amount of softener.

## (3.1) EFFECT OF HEAT

There is an increase in plasticity (decrease in  $y_5$ ) which is greater the higher the temperature of heating. The recovery and  $n$  are increased by heating up to 200° C, but more drastic heating (250° C) results in a decrease in both these values. There is a progressive decrease in molecular weight with increasing temperature of heating.

The results for the unextracted smoked sheet are complicated to some extent by the fact that a small amount of solid material distills off during the heating *in vacuo*. Tests showed that this material resembled the fat acids present in smoked sheet; in this connection the large increase in  $y_5$  on acetone-extracting smoked sheet (acetone extract 5.2 per cent) is noteworthy. The results for this acetone-extracted smoked sheet, and also for acetone-extracted latex rubber (not included in Table 1), show a similar increase in plasticity and increase in  $n$  and recovery on heating at 200° C, whence it may be concluded that the nonrubber components normally present in raw rubber does not fundamentally affect its behavior towards heat.

## (3.2) EFFECT OF OXIDATION

The plasticity is increased, while the recovery, and possibly also  $n$ , tend to increase in the initial stages of oxidation, although decreasing with prolonged oxidation, which also reduces the molecular weight, indicating scission of the

chains. The fact that the sample subjected to 1 day's oxidation showed a rather higher molecular weight than the untreated sample may be due to the smoked sheet not being homogeneous.

### (3.3) EFFECT OF MASTICATION

Both hot and cold mastication gave an increase in plasticity (decrease in  $y_s$ ), as expected, and a rapid decrease in recovery. Only hot mastication,

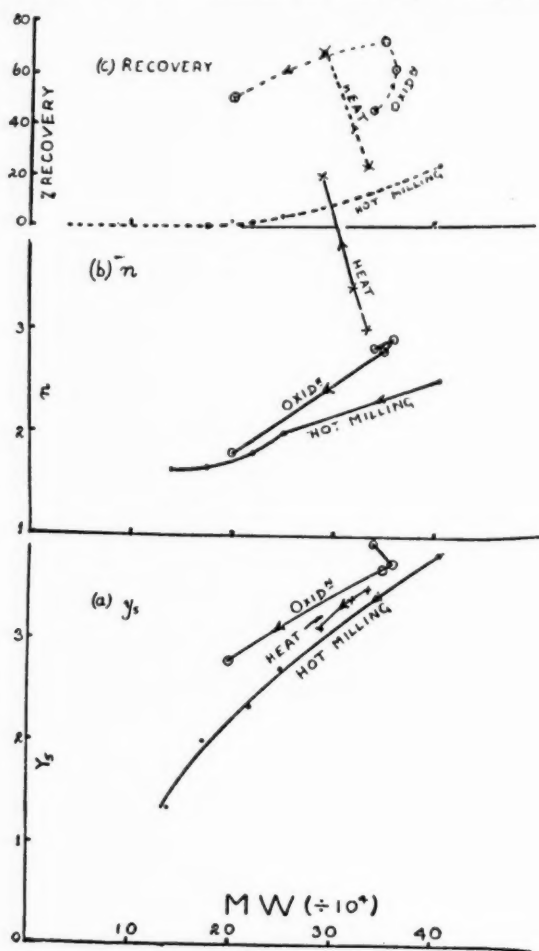


FIG. 2.—Relationship between molecular weight ( $MW$ ) and "softness" ( $y_s$ ),  $n$ , and recovery, for natural rubber subjected to various treatments.

however, seems to have reduced  $n$  to any great extent. Previous work<sup>15</sup> has shown that, with prolonged hot mastication,  $n$  eventually decreases to 1.0, *i.e.*, the value representing ordinary viscous flow.

Rubber containing an antioxidant (hydroquinone) is plasticized, by cold mastication, at the same rate as rubber without antioxidant. It must, there-

fore, be concluded that plasticization can be effected by purely mechanical means—presumably breakage of the rubber chain molecules, an effect considered more fully later<sup>17</sup>. This conclusion is confirmed by the fact that the nonoxidizable polyisobutene can be reduced in molecular weight by cold milling.

### (3.4) EFFECT OF SOFTENER

The rubber is progressively softened ( $y_5$  decreased) by increasing incorporation of oil. Examination of the complete plastometer data shows that neither the fluidity, *i.e.*, rate of flow under a constant shear stress, nor its reciprocal, the effective viscosity, changes proportionately to the amount of oil added; the increase in fluidity is approximately proportional to the square of the percentage of oil, while viscosity decreases most rapidly with the smallest additions, *e.g.*, 6 per cent of oil reduces the viscosity by more than half. The  $n$  value decreases when more than 10 per cent of oil is added; recovery shows a continuous decrease, particularly with the larger additions of oil.

### (3.5) COMPARISON OF PLASTICIZING TREATMENTS

The above results show that some degree of plasticization can be brought about by any one of the factors, heat, oxidation, and mechanical working, as well as by their combined action in ordinary hot mastication, and by incorporation of a softener such as mineral oil. It is now necessary to determine whether or not these four factors are equivalent in the sense of producing rubbers with identical plastic properties. To do this, Figure 1 has been prepared, in which  $n$  and recovery are plotted against what may conveniently be termed *softness*, as indicated by  $y_5$ .

It is at once evident that, in general, the five treatments have not produced the same effects, otherwise they would all be represented by curves of the same type. When rubber is softened, that is,  $y_5$  reduced, by hot milling,  $n$  and the recovery are likewise reduced, but when heat alone is used to soften the rubber, these properties at first increase greatly, making the rubber more nery, before they finally decrease. Oxidation reduces  $n$  but increases recovery, whereas mechanical working (cold milling) reduces recovery but seems to have little effect on  $n$ . Incorporation of oil at first softens the rubber without affecting  $n$ , but larger additions reduce this constant; recovery is reduced progressively as the rubber is softened, thus broadly resembling the effect of milling.

### (3.6) MECHANISM OF EFFECTS OBSERVED

The observed changes in plastic properties must be mainly due to:

- (1) breakage of the molecular chains into shorter lengths;
- (2) changes in the degree of intermolecular attachment by mechanical entanglements or chemical bonds (cross-linking);
- (3) the introduction of oxygen-containing groups that give rise to strong cohesive (van der Waals) forces;
- (4) changes in cohesive forces between the rubber chain molecules by introduction of oil molecules between them.

No information relating to (3) has been obtained in this preliminary investigation, but the molecular weight and  $n$  data give some information on (1) and (2).

The relation between molecular weight and plastic properties is shown in Figure 2. The trend of the  $y_6$  value with decreasing molecular weight is independent of the plasticizing method, so that this property seems to be essentially a function of molecular weight or chain length.

The relationships between  $n$  and recovery and the molecular weight, on the other hand, depend on the plasticizing method, showing that these properties are affected by other factors besides molecular weight. The dependence of  $n$  and recovery on molecular form is not well understood, nor is it clear to what extent these two properties are independent. Unpublished experiments (R.A.B.R.M.) with various synthetic rubbers have indicated a strong tendency for high values of  $n$  and recovery to be associated together, but their contrary behavior under certain treatments (see Figure 1) shows that they are not entirely interdependent.

The significance of  $n$  has been discussed by Houwink<sup>16</sup> and by Mark and Raff<sup>26</sup>, whose conclusions may be summarized as follows.

(1) Substances with globular molecules, *e.g.*, nonhardening resins, such as shellac and colophony, give  $n$  equal to 1, and so exhibit true viscous flow. In such substances the molecules adhere only by secondary (van der Waals) forces which are easily loosened by heat.

(2) Substances composed of chain molecules, *e.g.*, raw rubber, polystyrene, and polyvinyl acetate, may give  $n$  either equal to or greater than 1, depending on circumstances. These substances would be expected to have a tangled thread structure, so that the applied stress may have several functions to fulfil: disentangling the molecules from their neighbors, translation of the loosened molecules, and orientation of the molecules parallel to the direction of flow. If the molecular chains are not too long, *e.g.*, molecular weight not exceeding 50,000 for rubber<sup>16</sup>, the material gives  $n$  equal to 1 and so shows ordinary viscous flow, apparently because there is little intermolecular entanglement. With increasing chain-length the degree of entanglement increases<sup>27</sup>, and this leads to values of  $n$  greater than 1, so that the material exhibits quasi-flow; this type of flow is observed not only with rubber, but with other long-chain polymers, such as polystyrene and polyvinyl acetate. Parallel orientation of the molecules tends to reduce  $n$  towards unity, but this factor is probably not important in the parallel-plate test.

(3) Substances with cross-linked chain molecules presumably behave like those with entangled molecules, since in both cases the chains are joined together at intervals. This is confirmed by the observation that the scorching of rubber stocks containing sulfur and accelerators, which introduces sulfur cross-links, causes  $n$  to increase above unity.

On the basis of these views, the high  $n$  value for untreated rubber is due to the entanglements resulting from its very great chain length, and the reduction of  $n$  by hot milling is due to breakage of the chains into shorter lengths and loosening of the entanglements. The trend of the molecular weight/ $n$  curve for hot milling (Figure 2) is consistent with the observation<sup>16</sup> that  $n$  reduces to unity at a molecular weight of about 50,000. It is not clear, however, why cold milling has not produced the same effect as hot milling (see Figure 1).

The increase in  $n$  during heat treatment suggests cross-linking by C—C bonds, which has been claimed to occur under appropriate conditions of molecular activation<sup>18</sup>; cross-linking is indicated by the fact that some of the heated samples did not dissolve completely in benzene, since insolubility is a characteristic of cross-linked structures<sup>26</sup>. The decrease in  $n$  on passing to very high



temperatures may be ascribed to extensive breaking up of the cross-linked structure by chain scission.

Oxidation would be expected to attack the chains and break them into shorter lengths, but would not loosen the entanglements; on the other hand, cross-linking by oxygen bridges might occur<sup>18</sup>, so that the net result is difficult to predict.

Addition of oil would be expected to reduce  $n$ , since the oil itself has  $n$  equal to 1; the fact that the observed reduction is not proportional to the amount of oil is not surprising, since it has been shown in Section (3.4) that the effects of oil do not follow a simple mixture law.

The rapid decrease in recovery produced by hot or cold milling, compared with that produced by other plasticizing treatment, is noteworthy. The following explanation is put forward. The recovery of raw rubber depends partly on the existence of points of attachment within the network of rubber chains (Busse,<sup>19</sup> Treloar<sup>17</sup>). These points of attachment may consist of an interlocking of chains by secondary valence forces; or by mechanical entanglement, or both. During mastication, plastic flow in an extreme form takes place and a high strain is thrown on these attachments, which normally prevent or hinder plastic flow, and the links are broken. Thus mastication gives a rubber with a low recovery. In the oxidation of rubber, chain scission takes place, but no severe strain is thrown on the cross linkages or points of entanglement as in mastication, and hence recovery is not reduced to a low value. The effect of small amounts of oil in reducing recovery may be due to the oil molecules penetrating between the rubber chain molecules and so helping to loosen the entanglements.

The increase in recovery due to heating would result from the C—C cross-linking postulated above. The decrease at very high temperatures can be explained by the breaking up of the cross-linked structure into smaller and relatively compact, *i.e.*, not thread-like, molecules which would slip past each other readily and so without acquiring the internal strain that is the cause of recovery.

The mechanical breakage of the rubber chain-molecule introduces a chemical problem analogous to that of the end groups in the polyisoprene chain, because breakage leaves the atoms on either side of the broken link chemically unsaturated. The broken chain will thus be metastable, and the following possibilities may occur: (1) rearrangement of the links or atoms, possibly resulting in double bonds in the chain; (2) combination of the end groups with oxygen; (3) reunion of the end groups or reaction with the middle of another chain, forming a branched structure. The chemical structure of the chain thus has an important bearing on plasticization by milling. The reactivity of the broken ends may explain the function of certain chemical plasticizers in aiding mastication, namely, by combining with these end groups and so preventing their reunion with other end groups or chains.

It is interesting to consider the quantity of energy consumed in masticating rubber, and what becomes of this energy. To produce a well-masticated natural rubber requires the expenditure of about 0.5 kw.-hour per lb. If this energy were permanently taken up by the rubber molecule, the heat of combustion would be increased by nearly 1000 calories per gram. Actually, mastication does not affect the heat of combustion,<sup>20</sup> so this energy must be converted into heat, and as 1000 calories would raise the temperature of 1 gram of rubber to about 2000° C it is obvious that most of the heat must be conducted away by radiation and by the mill cooling water. Milling thus appears as a

very wasteful process, because practically all the energy consumed is converted into heat and lost.

#### (4) RESULTS FOR SYNTHETIC RUBBERS

The results for the butadiene-styrene and butadiene-acrylonitrile copolymers are shown in Table 2. They are confined mainly to the effect of heating *in vacuo*.

Experiments on heating Neoprene-E and Thiokol-F led to no useful result because at 200° C they partially decomposed, giving spongy masses together with a liquid distillate in the latter case.

##### (4.1) EFFECT OF HEAT

It will be observed that Buna-S has initially a low plasticity value (high  $y_5$  value). Heating both Buna-S and GR-S gives a product of lower plasticity ( $y_5$  increases) and much higher recovery, as well as increased  $n$  values.

The effect of heating the other butadiene copolymer—Hycar-OR—is similar. The plasticity decreases and recovery is increased from 58 to 95 per cent, indeed both this and Buna-S, after heating at 200° C, are almost perfectly elastic.

The following conclusions are indicated by the results: (1) butadiene-styrene and butadiene-acrylonitrile copolymers cannot be plasticized by heat alone; in this respect they differ from natural rubber, which shows softening when heated *in vacuo*; (2) in processing these types of synthetic rubber, application of heat in absence of oxygen or mechanical working should be avoided, as it causes stiffening and increases the nerve as indicated by the high recovery and  $n$  values.

The effect of heating *in vacuo* on the butadiene copolymers is attributed to cross-linking occurring between neighboring chains of the copolymer. This effect is similar to the effect of scorching on natural-rubber mixes. In support of this is the fact that, whereas GR-S is soluble in carbon tetrachloride, after heating it merely swells considerably in this solvent.

Cross-linking should result in a decrease in the chemical unsaturation and an attempt was made to confirm this by determining the iodine number of GR-S before and after heating at 150° C:

Iodine number before heating	317
Iodine number after heating at 150° C	318.5

There is thus no significant change. The matter is complicated by the fact that during heating the fat acids distil off from the rubber. The theoretical iodine number for the pure 75:25 butadiene-styrene copolymer is 352, or allowing for the impurities present in the crude copolymer, an iodine number of 330.5 is indicated for the latter. The crude GR-S is thus only slightly cross-linked.

##### (4.2) CROSS-LINKING IN TECHNICAL APPLICATIONS

The cross-linking produced by heat is a difficulty in several technical treatments and applications of the butadiene copolymers:

- (1) Thermal oxidative softening<sup>21</sup> of Buna-S and GR-S.
- (2) Reclaiming of vulcanizates made from the butadiene copolymers.
- (3) Heat aging of the vulcanizates during use or in accelerated aging tests.

In the thermal softening of Buna-S and GR-S, the softening due to oxidation occurs simultaneously with cross-linking due to the effect of heat alone. If the rubber is in compact form so that oxygen cannot readily penetrate to the interior, cross-linking will predominate. This is illustrated by comparative experiments with Buna-S and GR-S. The Buna-S was in the form of spongy crumb with a large surface, and thermal oxidation gave a soft plastic material with very low recovery and moderately low  $n$  value (see Table 2); in fact, a material not far removed in plastic properties from natural rubber masticated for 10–20 minutes; it was also very tacky. On the other hand, heating GR-S in the form of 0.5 inch thick slabs produced softening and tackiness on the surface only, and the tackiness almost disappeared in two days. By analogy with the results of Morgan and Naunton<sup>22</sup> for vulcanized rubber, high oxygen concentration and relatively low temperature, *i.e.*, slow oxidation, should give the greatest depth of oxygen penetration and hence the best plasticization. Reclaiming is essentially a replasticization of the vulcanizate, and if cross-linking can still occur after vulcanization, as the results of high-temperature aging tests<sup>23</sup> suggest, the above conclusion as to the effect of heat applies to reclaiming as well as to plasticization of the raw polymer. This is borne out by experiments on thermal reclaiming of GR-S<sup>24</sup>, which show that temperatures above about 150° C produce hardening, presumably due to cross-linking, though this might possibly be prevented by absorbed softeners if present in sufficient quantity.

The tendency towards cross-linking is a major defect of the butadiene-styrene copolymers, since it leads to considerable stiffening and loss of extensibility (heat embrittlement) when the vulcanizates are subjected to high temperatures<sup>23</sup>.

The present results emphasize the bad effect of allowing GR-S to become excessively hot when worked in an internal mixer, and particularly of allowing it to remain very hot after removal. The high temperature causes an increase in  $n$  and in elastic recovery, thus making the material tough and nervy. These undesirable changes are especially great when the material is at rest, since it seems likely that the continuous shearing action produced by the mixer to some extent prevents cross-linking, or at least breaks down the cross-linked structure into smaller, more mobile units.

##### (5) COMPARISON OF NATURAL AND SYNTHETIC RUBBERS

The effect on the plastic-flow properties of mastication is different in the two cases—natural rubber and butadiene-styrene copolymer.

Tables 1 and 2 show that masticating GR-S does not reduce  $n$  or the recovery so effectively as with natural rubber. Thus 20-minutes' mastication of GR-S gave a product having  $n = 3.0$  (or  $n = 4.3$  if masticated warm), while equivalent mastication of natural rubber gave a product having  $n = 1.64$ . Masticated GR-S thus gives a flow curve (rate of shear plotted against shear stress), strongly convex towards the stress axis and shows a correspondingly small flow at low shear stresses.

Some of the major difficulties in processing of Buna-S and GR-S, especially lack of tackiness or self-adhesion, have been ascribed by one of the present authors<sup>25</sup> to these differences in the plastic flow relations. Figure 3 shows the shearing stress plotted against the rate of shear for the above masticated rubbers. It is clear that, while at high stresses the rates of shear of the two rubbers may be approximately equal, with low stresses the rate of flow of masticated

GR-S may be less than one thousandth of that of masticated natural rubber. In the self-adhesion of unvulcanized rubber these flow properties appear to have an important influence for two reasons. (1) A good bond cannot be obtained unless the two surfaces make perfect contact at all points; this requires ability of the rubber to flow under the relatively small pressures applied in building up. (2) To avoid discontinuity at the boundary, it is necessary that

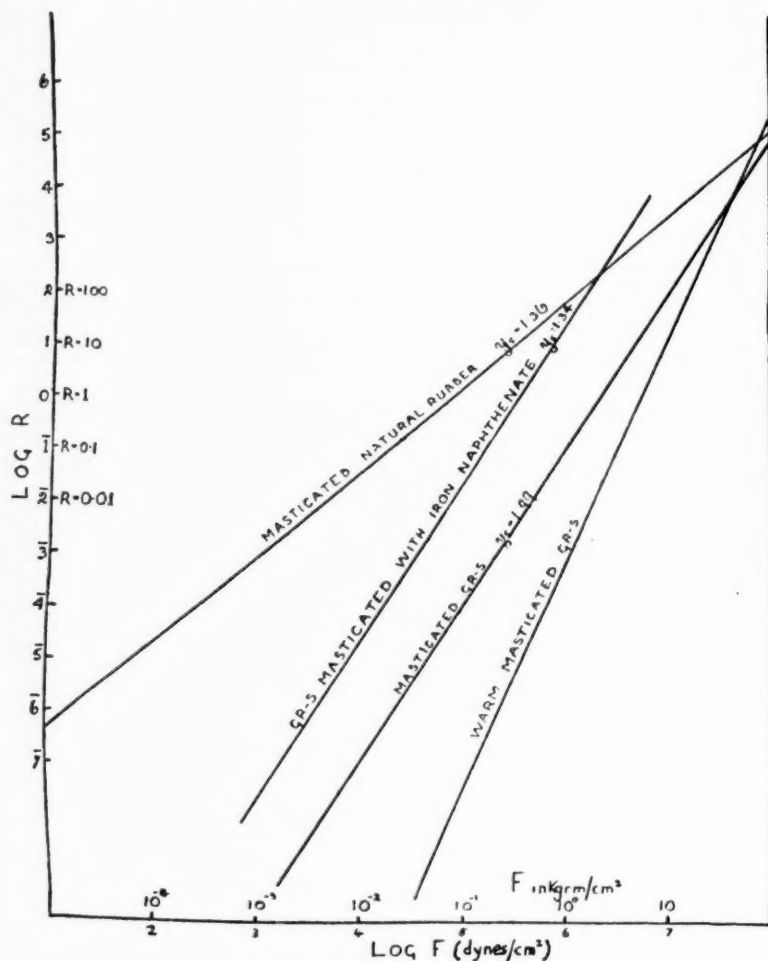


FIG. 3.—Relationship between shearing stress ( $F$ ) and rate of shear ( $R$ )

the long chains of rubber should be capable of diffusing to some extent from one surface into the other; this implies ability of the chains to flow under the very small stresses resulting from molecular agitation.

These considerations may explain the lack of adhesiveness of masticated butadiene-styrene rubbers, although a complete explanation of the phenomena of tackiness and adhesion would probably require also the forces of molecular

adhesion across the boundary to be brought into consideration. The explanation is supported by the fact that the tackiness of fresh thermally-softened Buna-S disappears in a few days concurrently with an increase in the recovery value. The plastic flow curves of Figure 3 relate to 90° C, but unpublished experiments (R.A.B.R.M.) show that at lower temperatures and low stresses the difference between the rates of flow for the two types of rubber is even more marked. This suggests that more satisfactory adhesion of GR-S stocks might be obtained by warming.

## REFERENCES

- <sup>1</sup> Scott, *Trans. Inst. Rubber Ind.* **20**, 8 (1944).
- <sup>2</sup> Piper and Scott, *J. Sci. Instruments* **22**, 206 (1945).
- <sup>3</sup> Porritt and Fry, *Trans. Inst. Rubber Ind.* **3**, 203 (1927).
- <sup>4</sup> Staudinger and Geiger, *Helv. Chim. Acta* **9**, 549 (1926).
- <sup>5</sup> Grenquist, *Ind. Eng. Chem.* **22**, 759 (1930).
- <sup>6</sup> Farberov and Margolina, *J. Rubber Ind. (USSR)* **12**, 230 (1935); *RUBBER CHEM. TECH.* **9**, 227 (1936).
- <sup>7</sup> Bolland and Orr, *Trans. Inst. Rubber Ind.* **21**, 133 (1945).
- <sup>8</sup> Cotton, *Trans. Inst. Rubber Ind.* **6**, 487 (1945).
- <sup>9</sup> Staudinger, *Ber.* **57**, 1203 (1924); *Ann.* **468**, 1 (1929); *Kolloid-Z.* **51**, 71 (1930).
- <sup>10</sup> Busse, *Ind. Eng. Chem.* **24**, 140 (1932).
- <sup>11</sup> Busse and Cunningham, *Proc. Rubber Tech. Conf. London*, **1938**, p. 288.
- <sup>12</sup> Callay, in "The Chemistry and Technology of Rubber," edited by Davis and Blake, New York, **1937**, p. 150.
- <sup>13</sup> Kemp and Peters, *J. Phys. Chem.* **43**, 1063 (1939); *Ind. Eng. Chem.* **33**, 1391 (1941); Bloomfield and Farmer, *Trans. Inst. Rubber Ind.* **16**, 69 (1941).
- <sup>14</sup> Blake and Bruce, *Proc. Rubber Tech. Conf. London*, **1938**, p. 736.
- <sup>15</sup> Scott, *Trans. Inst. Rubber Ind.* **7**, 169 (1931); **10**, 481 (1935).
- <sup>16</sup> These determinations were made by the British Rubber Producers' Research Association.
- <sup>17</sup> In the section on the "Mechanism of Effects Observed".
- <sup>18</sup> Houwink, "Elasticity, Plasticity, and the Structure of Matter", Cambridge, **1937**.
- <sup>19</sup> Mark and Raff, "High Polymers", Vol. 3, p. 28.
- <sup>20</sup> Gee and Treloar, *Trans. Inst. Rubber Ind.* **16**, 184 (1940).
- <sup>21</sup> Staudinger, *Proc. Rubber Tech. Conf. London*, **1938**, p. 253.
- <sup>22</sup> Busse, *J. Phys. Chem.* **36**, 2862 (1932); Staudinger, *Proc. Rubber Tech. Conf. London*, **1938**, p. 253; Treloar, *Trans. Faraday Soc.* **36**, 538 (1940).
- <sup>23</sup> Messenger, *Trans. Inst. Rubber Ind.* **5**, 71 (1929).
- <sup>24</sup> Hagen, *Kautschuk* **14**, 203 (1938); Koch, *Ind. Eng. Chem.* **32**, 464 (1940).
- <sup>25</sup> Morgan and Naunton, *Proc. Rubber Tech. Conf. London*, **1938**, p. 599.
- <sup>26</sup> Newton, unpublished work of the Research Assocn. of British Rubber Manufrs.; Scott, *Trans. Inst. Rubber Ind.* **21**, 78 (1945).
- <sup>27</sup> Fisiz, unpublished work of the Research Assocn. of British Rubber Manufrs.; United Kingdom Ministry of Supply, Advisory Service on Rubber. "Utilization of Synthetic and Natural Rubber Waste", Circular No. G-4, 1946.
- <sup>28</sup> Scott, *Trans. Inst. Rubber Ind.* **20**, 8 (1944).
- <sup>29</sup> By the Research Assocn. of British Rubber Manufrs.

# STATISTICAL ANALYSIS OF PLASTICITY MEASUREMENTS OF NATURAL AND SYNTHETIC RUBBER \*

M. C. THRODAHL

RUBBER SERVICE DEPARTMENT, MONSANTO CHEMICAL CO., NITRO, WEST VIRGINIA

## INTRODUCTION

The reliability of plasticity data on rubber is affected by (1) variance in precision of measurement by the instrument used and (2) heterogeneity of the rubber. While the relative precision of the instrument and observer error must be considered, the problem is somewhat complicated by the fact that each sample is used only once. Thus a single measurement is made on  $n$  like things rather than  $n$  like measurements on a single thing. Methods commonly used are the Williams parallel-plate<sup>1</sup>, Dillon and Johnston extrusion<sup>2</sup>, and Mooney shear<sup>3</sup>.

Rather meager data have been published on plasticity measurements of large numbers of samples (200-300) of elastomers. Riebl<sup>4</sup> and Martin, Davey and Baker<sup>5</sup> have reported no dispersion values, only averages of  $D_{30}$  plasticity values of smoked sheet and crepe being shown, using a parallel-plate plastometer. Aside from Mooney plasticity values of GR-S on 45-50 samples given in recent papers by Heide<sup>6</sup> and Vila and Gross<sup>7</sup> no statistical data for GR-S plasticity are available in the literature.

It is the purpose of this paper to present a simple statistical analysis of the three types of plasticity measurements for GR-S and natural rubber (Hevea smoked sheet) based on 256 specimens.

## EXPERIMENTAL

The three standard plastometers<sup>8</sup> were used under the conditions set forth in Table I. GR-S specimens were prepared from randomly selected 100-gram

TABLE I  
PLASTOMETERS USED AND CONDITIONS OF TEST

Type	Conditions
Williams	5 kg. load, 2 cc. specimen, 100° C temperature, 6 minutes preheat.
Extrusion	<p>GR-S</p> <p>(0.703 kg. per sq. cm.) 10 lb. per sq. in. air pressure, six minutes preheat at 90° C in air. Running temperature of 82° C, one minute preheat in plastometer.</p> <p>Smoked Sheets (Hevea)</p> <p>(0.843 kg. per sq. cm.) 12 lb. per sq. in. air pressure, six minutes preheat at 82° C. Running temperature of 82° C, one minute preheat in plastometer.</p>
Mooney	One minute preheat at 100° C; reading taken after four minutes running, using large rotor.

\* Reprinted from the *Journal of Colloid Science*, Vol. 2, No. 1, pages 187-191, February 1947.



pieces cut from a single 75-pound bale (U. S. Rubber Co., Institute, W. Va.). These were milled for eight minutes on a 6 × 12 inch mill at a 45° C roll temperature, using an 0.08 nip width. Each piece was sufficient for two extrusion specimens rolled into cylindrical form from very thinly sheeted stock. Specimens were cut to weight 19 grams. Owing to the high shrinkage of GR-S, these were made up 15 minutes before preheating, wrapped in varnished cambric and held together tightly with rubber bands. Mooney slabs were prepared according to the method of Taylor<sup>9</sup> from GR-S milled in the manner previously described. Williams pellets were drilled from a 500-gram milled slab. Smoked-sheet specimens were prepared from randomly selected 100-gram milled slab. Smoked-sheet specimens were prepared from randomly selected 100-gram pieces cut from a 250-pound bale. A total of 2500 grams was masticated 5 minutes in a type OO Banbury mixer running 76 r.p.m. at a stock temperature of 80° C. This masticated batch was divided into 5 parts and further mixed 2 minutes on the mill. Sheeted stock was plied up evenly to a thickness necessary for each type of specimen. Extrusion and Williams specimens were bored from thick slabs, using a cork borer fitted to a power drill. Mooney slabs were cut from stock sheeted off to the desired thickness. Preparation of specimens was as previously described.

## RESULTS AND DISCUSSION

All statistical quantities shown in Table II were calculated from equations commonly expressed in any standard reference on mathematical statistics. A

TABLE II  
STATISTICAL QUANTITIES FOR TWO SETS OF PLASTICITY MEASUREMENTS  
ON DIFFERENT LOTS OF HEVEA (SMOKED SHEET) AND GR-S

Set 1		Williams							
Number of specimens	Statistical quantity	Hevea		GR-S		Extrusion		Mooney	
		$Y_1$	$Y_{\infty}$	$Y_1$	$Y_{\infty}$	Hevea	GR-S	Hevea	GR-S
256	$\bar{X}$	272.6	385.5	343.5	464.3	48.5	18.6	79.5	48.7
	$0.01 \sigma \bar{X}$	4.6	4.1	3.5	8.3	2.7	0.7	0.3	0.3
	$\sigma^2$	806.0	642.0	468.0	2586.3	282.0	18.7	3.8	4.28
	$\sigma$	28.4	25.3	21.6	50.9	16.8	4.3	1.95	2.06
	$\sigma \bar{X}$	1.78	1.58	1.35	3.18	1.05	0.27	0.12	0.13
	$V$	10.4	6.6	6.3	10.9	34.6	23.1	2.4	4.2
Set 2									
25	$\bar{X}$	467.2	795.0	396.0	949.0	73.0	26.2	96.3	68.9
	$\sigma^2$	300.9	3453.3	79.4	9415.0	79.9	12.3	0.8	0.6
	$\sigma$	17.3	58.8	8.9	97.0	8.9	3.5	0.9	0.8
	$\sigma \bar{X}$	3.46	11.80	1.78	19.45	1.79	0.70	0.18	0.16
	$V$	3.7	7.4	2.3	10.3	12.2	13.3	0.9	1.1

value of  $t_{0.01}$  of 2.597 derived from the Normal Law Integral was taken from a table<sup>10</sup> of values of  $t$ .

In parallel-plate plasticity, the thickness of the specimen is read at different times, plasticity being denoted by  $K$  in the following equation:

$$K = Yx^n,$$

where  $Y$  is the specimen thickness,  $x$  is time in minutes and  $n$  is a constant. According to Williams<sup>1</sup> the data fit the theoretical curve fairly well at  $Y$  values taken at approximately three minutes. The curve is tangent to the  $x$  and  $y$

axes at infinity but, since the specimen originally has measurable thickness, the readings taken over the first very short interval do not fall along the curve. To test this, appropriate  $Y_{0.5}$  and  $Y_3$  readings were taken for each specimen along with the  $Y_5$  values. Frequency distribution of the  $Y_{0.5}$  values (not given here) showed that they had but slight tendency to group themselves about a central mean in a symmetrical manner which would allow use of normal error law treatment. The  $Y_3$  values were considerably more precise than the  $Y_{0.5}$ , but were not used—the  $Y_5$  values being preferred.

The data indicate that the Mooney plasticity data are the most precise, with Williams plasticity data reasonably close. The extrusion data showed that this type of measurement has the greatest variability; precision was affected appreciably by the less effective temperature control<sup>11</sup>.

Surprisingly the coefficient of variability was less for GR-S than for Hevea in the Williams and extrusion plastometer measurements. The Mooney values, however, were more precise for Hevea than for GR-S.

Probably the most significant factor influencing the results was the cleanliness of the rubber chambers of the extrusion and Mooney plastometers, especially with the latter. It was found, for example, that meticulous care was necessary in punching the proper sized hole in the Mooney specimen for the rotor, otherwise the rubber would work between the rotor shaft and its bearing, causing wild fluctuation of the dial gauge. This may have occurred occasionally during the running of the series; however, after 256 readings the instrument was dismantled and inspected for collected rubber. None was found.

#### ADDENDUM

Mooney has suggested to the author that, in addition to the precision measures employed in the paper, a rating of practical significance would be one based on the "... ability of the instrument to distinguish between two samples which are not very different". Thus, both methods of rating would give the same relative standing only if the same percentage difference existed between two different samples, by different methods.

To apply this suggestion, a group of 25 samples were prepared from a different lot of Hevea and GR-S (the GR-S used was of an experimental type of known divergence from regular GR-S) in a similar manner and tested as before. The various statistical calculations are shown in set 2 of Table II.

Mooney used the term *coefficient of discrimination* as applied to a specific test for two specific samples and defined it as:

$$D = \frac{\bar{X}_1 - \bar{X}_2}{\sigma},$$

where  $\bar{X}_1 = \bar{X}$  arithmetic mean for samples of set 1,  $\bar{X}_2$  = arithmetic mean for samples of set 2,  $\sigma$  = standard deviation within samples which would be calculated from:

$$\sigma = \sqrt{\frac{n_1\sigma_1^2 + n_2\sigma_2^2}{n_1 + n_2}},$$

where  $n_1$  and  $n_2$  are the numbers of measurements in the respective samples and  $\sigma_1^2$  and  $\sigma_2^2$  are the respective variances. To illustrate, typical values are tabulated from the calculations supplied by Mooney.

Discrimina- tion between sets of samples	Williams				Extrusion		Mooney	
	Hevea		GR-S		Hevea	GR-S	Hevea	GR-S
	$Y_1$	$Y_\infty$	$Y_1$	$Y_\infty$				
	$D_{1-2}$							
	7.1	13.7	2.5	8.6	1.5	1.8	8.9	10.2

These show that the extrusion plastometer has less discriminating ability than the others. However, as Mooney has pointed out, this is not as low as the precision measures indicate. These results lead to a somewhat different conclusion from that reported by Dillon<sup>12</sup>, who used the term *selectivity* (percentage difference between two observations on different mixtures divided by the average maximum percentage error), and found that the extrusion plastometer ranged from twice to twenty times that of the Williams plastometer when the two instruments correlated. When they failed to correlate, the relative sensitivity of the two instruments had no meaning.

## REFERENCES

- <sup>1</sup> Williams, *Ind. Eng. Chem.* **16**, 362 (1924).
- <sup>2</sup> Dillon and Johnston, *Physics* **4**, 225 (1933); RUBBER CHEM. TECH. **7**, 248 (1934).
- <sup>3</sup> Mooney, *Ind. Eng. Chem., Anal. Ed.* **6**, 147 (1934).
- <sup>4</sup> Riehl, *Arch. Rubbercultuur* **14**, 223 (1930); Van Rossem, in "The Chemistry and Technology of Rubber", edited by Davis and Blake, New York, 1937, p. 53, Table 34.
- <sup>5</sup> Martin, Davey and Baker, Rubber Research Scheme (Ceylon), Bull. No. 52, Peradeniya (1932); Dawson and Porritt, "Rubber: Physical and Chemical Properties", Research Assoc. Brit. Rubber Manufs., Croydon, 1935, p. 48, Table 194.
- <sup>6</sup> Heide, *India Rubber World* **114**, 653 (1946).
- <sup>7</sup> Vila and Gross, *Rubber Age* (N.Y.) **57**, 551 (1945).
- <sup>8</sup> Williams, *Ind. Eng. Chem.* **16**, 362 (1924); Dillon and Johnston, *Physics*, **4**, 225 (1933); RUBBER CHEM. TECH. **7**, 248 (1934); Mooney, *Ind. Eng. Chem., Anal. Ed.* **6**, 147 (1934).
- <sup>9</sup> Taylor, Natl. Bur. Standards, Circ. C-451 (Nov. 8, 1945).
- <sup>10</sup> Snedecor, "Statistical Methods", Iowa State College Press, Ames, 1946, p. 65, Table 3.8.
- <sup>11</sup> Special installation of Superior Electric Co. Powerstats for this instrument have held the temperature change over a range of about  $\pm 4^\circ$  C.
- <sup>12</sup> Dillon, *Physics* **7**, 73 (1936); RUBBER CHEM. TECH. **9**, 496 (1936).

# METHOD OF TESTING THE MECHANICAL PROPERTIES OF VULCANIZATES PREPARED FROM LATEX AS A STARTING MATERIAL \*

MARCEL PIROT

TECHNICAL STAFF, SOCIÉTÉ DE PLANTATIONS DES TERRES ROUGES, INDOCHINA

## GENERAL PRINCIPLES

The method used in the present work is that of Minatoya and Iguti<sup>1</sup>, which has been improved by Chalmeau<sup>2</sup>. In this method the deposit of rubber obtained by dipping a hollow tube into latex is rolled up into the form of rings. For the dipping operation, the laboratory device described by Flint<sup>3</sup> was adopted. The operating technique was as follows.

Aluminum tubes closed at their upper ends were first dipped into the latex mixture. The assembly used for dipping (see Figure 1) was made up of a

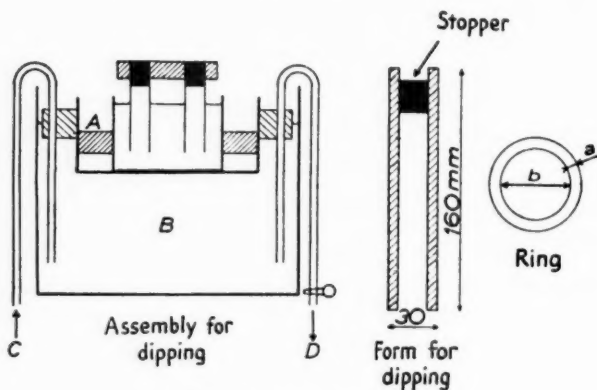


FIG. 1.—Testing equipment.

removable tank, containing the latex mixture, which floated in a reservoir B, the contents of which could be siphoned away. Any other method whereby the rate of ascent and descent of the tank can be regulated should be satisfactory.

After the dipping operation, the forms are dried in an oven at 25–30° C. Drying to constant weight is accomplished in about one-half hour, and is evident by the entire surface of the film of rubber becoming transparent. The thickness of this film is then of the order of 0.04 mm. The forms are dipped very rapidly in benzene, the solvent is allowed to evaporate, and the film is rolled up. In this way a ring-shaped test-specimen is obtained, which is then vulcanized.

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 23, No. 2, pages 28–33, February 1946.

## DETAILS OF THE PREPARATION OF TEST-SPECIMENS

The latex bath was prepared in such a way that the deposit on the dipping form had, after drying, the following compositions:

Rubber	100
Sulfur	2
Sodium dimethyldithiocarbamate <sup>4</sup>	1
Zinc oxide	3

The sulfur and zinc oxide were added in the form of dispersions to the latex. These dispersions were prepared in the usual way; *i.e.*, on the one hand from a mixture of 100 parts of sulfur, 20 parts of a 4 per cent solution of tragacanth gum, 2 parts of Distabex-L<sup>5</sup>, and 118 parts of water, and, on the other hand, 100 parts of zinc oxide, 30 parts of a 4 per cent solution of tragacanth gum, 3 parts of Distabex-L and 167 parts of water. Ordinary flowers of sulfur and ordinary zinc oxide were used in preparing these dispersions; the tragacanth gum should be of high quality and in the form of whitish, translucent pieces. A soluble accelerator was chosen purposely, since it has been found by experience that good reproducibility of results is difficult with insoluble accelerators. The accelerator was added in the form of a 15 per cent solution to the latex mixture.

Aluminum forms were used instead of glass tubes, for it is difficult to obtain a large number of glass forms with the same diameters and, since this factor plays a part in calculating the cross-section of the final ring test-specimen, it is advisable to use identical forms for dipping. It is advantageous also to use several forms simultaneously, and it is important that the forms are held in a strictly vertical position.

The rate of descent of the tank influences the thickness of the film of latex deposited, *i.e.*, the greater the rate, the thicker is the resulting film, and conversely. This rate of descent can be utilized to compensate for the differences in thickness of a film resulting from differences in the viscosity of latices and in this way to obtain ring test-specimens having cross-sections of similar dimensions. It will be shown later that this condition should be fulfilled, failing which another cause of variability in the tensile strength is introduced. Another factor which can be controlled is the depth to which the tubes are dipped, for the deeper they are dipped, the larger is the torus cross-section for a given thickness of film. However, it is more practical to keep this factor constant, and in experiments which are to be described a depth of dipping of 7 cm. was adopted. The depth of the latex in the tank should exceed the depth of dipping by an amount which depends on the number of rings which are to be prepared.

After the drying operation, the rubber film is no longer sticky, and if it is rolled up just as it is, a ring is obtained with a laminated structure which persists after vulcanization. For this reason the forms are dipped in benzene, so that the film becomes tacky, and when it is rolled up the different layers adhere to one another. Vulcanization then increases this adhesion. It may happen, however, that the adhesion is not perfect at all points. Nevertheless it has been found that these imperfections do not have any serious effect on the reproducibility of the results, which is the most important aim.

The rubber films were at first rolled up by hand. However, with this manual operation it was impossible to roll up a film progressively so as to form a torus of uniform dimensions at all points of the circumference, and this led to a certain distortion, with a tendency for the ring to roll itself into the form of a figure 8. An improved way was found to be to start the rolling by hand and then to insert the tube into a rubber sleeve, 0.25 mm. thick, having an

internal diameter equal to the external diameter of the aluminum tube. The rubber sleeve caused the deposited film to roll up on the form uniformly at all points of the circumference. It was found that it is preferable not to move the rubber sleeve by a steady motion, but to move it by successive impulses with a back-and-forth motion. For greater ease of operation, the rubber sleeve was mounted at one end of a rigid support which may be, for example, a napkin ring (see Figure 2).

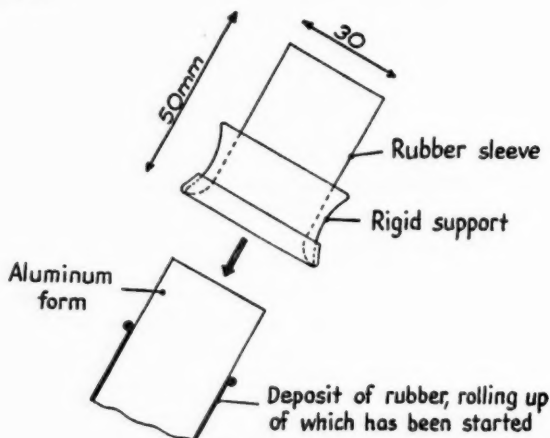


FIG. 2.—Equipment for rolling up rings.

Vulcanization was at first carried out in an oven at 100°, for a period of 45 minutes. However, the temperature of an ordinary oven is never uniform, and a special vulcanizing chamber was designed (see Figure 3). This consists of

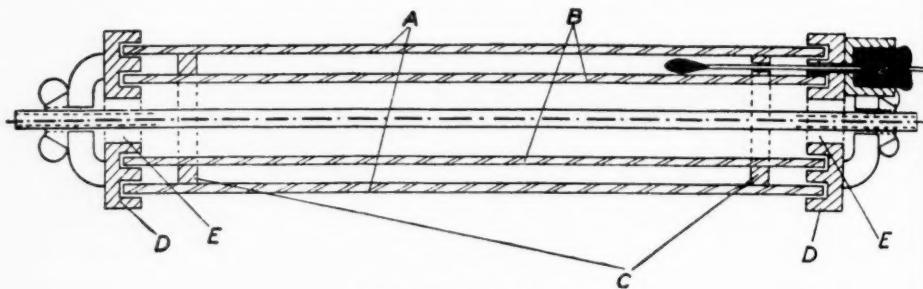


FIG. 3.—Vulcanizing chamber.

two concentric aluminum tubes, A and B, centered on each other by discs C. The space between the two tubes is 5 mm. The inside tube has an external diameter of 25 mm., the outside tube an internal diameter of 35 mm. The ring test-specimens are slipped on the inner of the two tubes. The two ends are closed by the end plates D, each of which has a center opening E, 10 mm. in diameter. When placed in boiling water, this assembly has the advantage of both external and internal circulation of water and, as a result, the temperature increases rapidly within the chamber (less than three minutes), and the best conditions for a constant and at the same time uniform temperature are maintained.



Since the diameter of the ring test-specimens is a little less than the outside diameter of the central tube on which they are placed, vulcanization takes place with the rings under slight tension; as a result the vulcanized rings are perfectly circular. With this equipment, the optimum state of cure of the rubber mixture shown above is reached in 15 minutes.

*Determination of the cross-section.*—The cross-section of the torus is given by the relation: (1)  $S = \frac{V}{2\pi R}$ , where  $V$  is the volume of the torus and  $R$  is the radius of the circle described by the center of gravity. The volume is a function of the weight  $W$  and density  $d$ , so relation (1) becomes: (2)  $S = \frac{W}{2d\pi R}$ .

In a tensile test, the double section must be taken into account: (3)  $S = \frac{W}{d\pi R}$ .

The density of rubber is considered to be 0.96. To estimate  $R$ , the thickness  $a$  and inside diameter  $b$  of a large number of rings are measured with a microscope, the movement of whose slide could be measured. The measurements are made in two perpendicular directions. The mean value of  $a$  was found to be 1.72 mm., and of  $b$  24.5 mm.

$R$  is therefore equal to  $\frac{24.5 + 1.72}{2} = 13.11$  mm., and the relation (3) becomes  $S = \frac{P}{0.96 \times 3.14 \times 13.11} = \frac{P}{39.48}$ .

The straight line  $y = \frac{x}{39.48}$  can then be plotted, and the double section obtained as a function of the weight. Finally it is necessary only to measure  $W$  to obtain the required cross-section.

## EXPERIMENTAL PART

### VERIFICATION OF THE FORMULA FOR DETERMINING THE CROSS-SECTION

It is indispensable to verify the formula for determining the cross-section. To this end the thickness  $a$  was measured microscopically at four different points, viz., at the four extremities of the two orthogonal diameters. From the values it was possible to calculate the double section  $S$ . Table 1 shows the values of  $S$  obtained by the formula and by means of the microscopic technique.

TABLE 1

Weight (mg.)	$S$ (by formula) (sq. mm.)	$S$ (microscopically) (sq. mm.)	Difference (sq. mm.)
186	4.7	4.9	0.2
195	4.9	4.7	0.2
200	5.0	5.0	0.0
165	4.1	4.1	0.0
175	4.4	4.3	0.1
166	4.2	4.1	0.1
156	3.9	4.0	0.1
162	4.1	3.7	0.4
161	4.1	4.0	0.1
155	3.9	3.8	0.1
165	4.1	4.1	0.0
	$M = 4.31$	$M = 4.24$	$M = 0.1$

The difference which was found between the values for the cross-section obtained by the two methods is small—2.3 per cent in this particular case. The differences are attributable to the fact that the number of measurements made by the microscopic technique are too small; however, they are small enough to warrant the conclusion that the formula is satisfactory.

#### RESULTS OBTAINED WITH CONCENTRATED LATEX

##### *Rate of dipping*

As has already been pointed out, the rate of descent of the tank influences the thickness of the deposited film and, therefore, also the weight of the ring. Table 2 shows the weights obtained after different times of dipping. It will be seen that these weights increase with shortening of the time of dipping.

TABLE 2

Time of dipping		Weight (mg.)
Min.	Sec.	
3	30	173
1	0	265
0	54	345
0	45	338

However, it is also evident that, at least for the latex mixture tested, a point is reached in shortening the time below 1 minute where no further increase in thickness can be obtained by further shortening of the time of dipping. It should also not be forgotten that rapid dipping results in the latex flowing on the forms, and any satisfactory technique is necessarily a compromise between these two facts.

#### INFLUENCE OF THE VISCOSITY

Latex mixtures thicken in the course of time, from the action of both zinc oxide and of accelerator. This change is manifest in the results obtained in the dipping operation. Table 3 gives an indication of this thickening of a latex mixture; here the weights given are the mean values of several series of rings. The time of dipping was 45 seconds.

TABLE 3

Weight (mg.)	Age of mixture (days)
365	5
391	7
396	9

A further series of experiments, shown graphically in Figure 4, indicates that, although the increase in viscosity as a function of time increases the weight of the resulting rings, this increase in viscosity does not have any significant effect on the tensile strength.

#### INFLUENCE OF THE CROSS-SECTION OF THE RING

In spite of the fact pointed out in the preceding paragraph, the tensile strength is influenced by relatively small differences in cross-section of the ring test-specimens, probably because the poor heat conductivity of the rubber mix-

ture results in different states of cure at the center of the cross-section and at its periphery. Table 4 gives the tensile strengths obtained with different ring test-specimens as a function of their cross-section.

TABLE 4

Cross-section (sq. mm.)	Tensile strength (kg. per sq. cm.)
6.6	400
6.9	400
7.6	390
9.2	340
9.9	335
10.0	330

The tensile strength decreases considerably when the cross-sectional area is 8–9 sq. mm. or more, whereas it is approximately the same for smaller cross-sections. This explains the results obtained in studying the influence of viscosity, when the cross-sectional areas were 5.8 to 7.3 sq. mm.

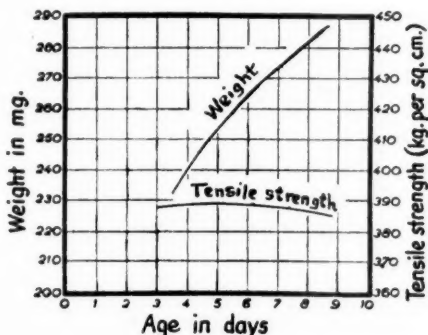


Fig. 4.—Influence of the age of a latex mixture on the weight of a ring prepared from it and on the tensile strength of the ring.

One is led to the conclusion from these observations that it is necessary to test specimens, the cross-sectional areas of which are similar, but that the tolerance is sufficiently large to make it possible to use satisfactorily rings within the practical limits of 5.5 to 7.5 sq. mm.

#### DETERMINATION OF THE OPTIMUM STATE OF VULCANIZATION

*Vulcanization in an oven at 100° C.*—Figure 5 shows tensile strength as a function of the time of vulcanization<sup>6</sup>, and also that the optimum state of cure was reached in 45 minutes. However, this cure was not uniform because of differences in temperature within the oven. In a series of one-hundred rings, vulcanized in four groups in this way, it was not possible to obtain results sufficiently well grouped to calculate statistically the most probable mean value.

*Vulcanization in the new apparatus.*—The use of the vulcanizing chamber immersed in boiling water made possible much more rapid vulcanization, as is evident from the data in Figure 6, which show that the optimum state of vulcanization was reached in 15 minutes.

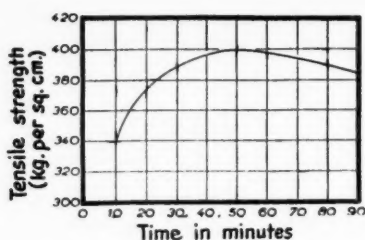


Fig. 5.—Curve of vulcanization in an oven at 100° C.

## INFLUENCE OF THE TIME OF DRYING OF THE RUBBER FILM AFTER DIPPING

The importance of thorough drying of the rubber film is seen in Figure 7, the graph of which represents tensile strength as a function of the time of

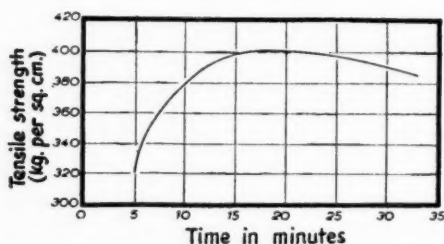


Fig. 6.—Curve of vulcanization in the special chamber.

drying of a film formed by the dipping operation. These tests were made on rings which had been vulcanized in an oven for 30 and 45 minutes. This curve shows that drying for about 30 minutes seemed to be the most favorable condition. In this case the drying was carried out in an oven at 25–30° C.

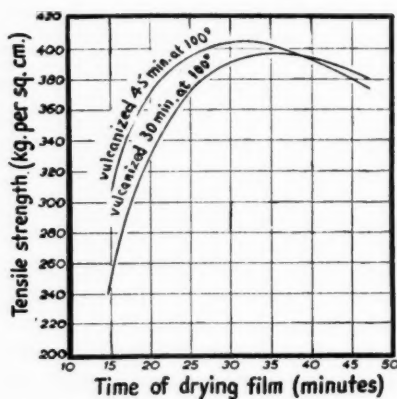


Fig. 7.—Influence of the time of drying on the tensile strength.

## TENSILE STRENGTH AND MODULUS INTERPRETATION OF THE RESULTS

As the data in Figures 5, 6 and 7 indicate, the optimum tensile strength was of the order of 400 kg. per sq. cm.; the modulus at 700 per cent elongation was approximately 200 kg. per sq. cm., and the rings broke at 800 per cent elongation.

These high values for the tensile strength and for the modulus can be explained in at least two ways. First, they were obtained with vulcanizates prepared from latex, and it is a known fact that such mixtures have higher tensile strengths than corresponding crude-rubber mixtures which have been put through the milling operation. Secondly, ring test-specimens, with their circular cross-section, do not show the same tendency to start breaking as do rings or other types of test-specimens which have been died out and have rectangular cross-sections.

In this work it was necessary also to estimate the reproducibility of the results. To this end statistical calculations were applied to tensile strength and modulus data obtained by testing a series of one hundred rings. Since this calculation is valid only if the distribution of the results concerned is at random, it was necessary first of all to demonstrate that the distribution curve is of the type of a Gauss curve. The adjustment curve showed that, by eliminating one single value in the hundred which was considerably lower than all the others, the distribution of the tensile strength and modulus values approached a state of random distribution.

Figures 8 and 9 are histograms and theoretical frequency curves of the two populations studied.

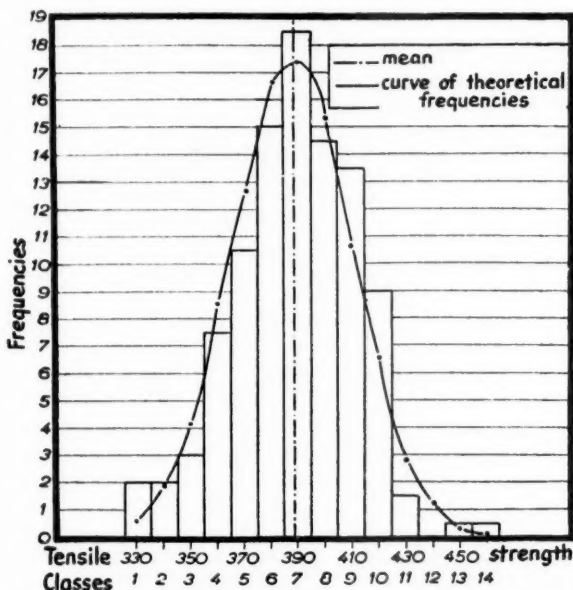


FIG. 8.—Histogram and theoretical frequency curve of the tensile strength.

For the tensile strengths,  $P$  is equal to 0.7–0.8; for the modulus values, it is 0.2–0.3. Since the lower limit of  $P$  which is compatible with a Gauss curve is 0.05, it is evident that the values obtained for  $P$  are good<sup>7</sup>.

It is possible, then, to utilize the ordinary factors of normal distributions, including  $M$ ,  $\sigma$ , and  $\sigma_m$ .

$M$  is the arithmetic mean, and is calculated by the formula:  $M = \frac{\sum x}{n}$ , where  $x$  represents the individual values and  $n$  the number of tests.

$\sigma$ , or standard deviation, is represented by the formula:  $\sigma = \frac{\sqrt{\sum (x - M)^2}}{n - 1}$

and it defines on both sides of the mean value a zone comprising 68 per cent of the results. If, instead of  $\sigma$ ,  $2.575\sigma$  is considered, the delimited zone comprises 99 per cent of the results.

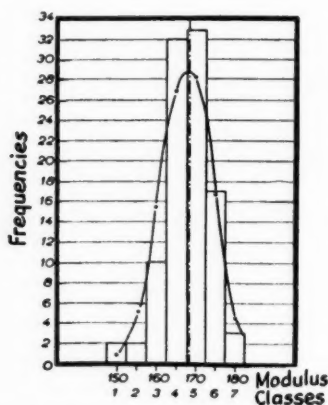


Fig. 9.—Histogram and theoretical frequency curve of the modulus at 700 per cent elongation.

The arithmetic mean found involves an error as a result of the fact that an infinite population has not been considered. This standard deviation of the mean, or  $m$ , is equal to:  $\sigma_m = \frac{\sigma}{\sqrt{n}}$ . It can be shown that the true mean of an infinite population has 99 chances in 100 of being between  $M - 2.575\sigma_m$  and  $M + 2.575\sigma_m$ .

From the practical point of view it is of interest in the case under consideration to know the precision of the mean of ten tests (frequently the number of test-specimens which are tested). This is why  $\sigma_{10}$  is calculated as equal to  $\sigma\sqrt{10}$ .

Evidently  $\sigma_{10}$  is greater than  $\sigma_m$ , for the smaller the number of tests, the smaller the chance that their mean value approaches the true mean value.

Table 5 summarizes the values obtained for the various parameters applied to the populations in question.

The data in Table 5 show that with respect to the tensile strength: (1) the mean value is 388 kg. per sq. cm.; (2) 68 per cent of the results lie between 366 and 410 kg. per sq. cm.; 99 per cent of the results lie between 332 and 444 kg. per sq. cm.; (4) the true mean of 100 breaks has 99 chances in 100 of lying between 382.4 and 393.6 kg. per sq. cm., and (5) with 10 tests the true mean has 99 chances in 100 of lying between 369.7 and 406.2 kg. per sq. cm.

With respect to modulus: (1) the mean value is 167.8 kg. per sq. cm.; (2) 68 per cent of the results lie between 161.1 and 174.5 kg. per sq. cm.; (3) 99 per



TABLE 5

Parameter	Tensile strength (kg. per sq. cm.)	Modulus (kg. per sq. cm.)
$M$	388	167.8
$\sigma$	22	6.75
$2.575\sigma$	56	17.4
$m$	2.2	0.65
$2.575\sigma_m$	5.6	1.7
10	7.1	2.2
$2.575\sigma_{10}$	18.3	5.6

cent of the results lie between 150.4 and 185.2 kg. per sq. cm.; (4) the true mean of 100 breaks has 99 chances in 100 of lying between 166.1 and 169.5 kg. per sq. cm., and (5) in 10 tests, the true mean value has 99 chances in 100 of lying between 369.7 and 406.3 kg. per sq. cm.

It will be seen that the limits between which the true mean values of ten tests tend to vary are approximately 10 per cent for tensile strength and approximately 6 per cent for modulus.

#### REPRODUCIBILITY OF THE RESULTS FROM ONE MIXING TO ANOTHER

In the preceding section the reproducibility of results obtained from rings prepared from the same mixture is discussed. It is necessary likewise to study the reproducibility of results obtained with rings of the same composition but prepared at different times. The results obtained by this method are reproducible also with rings prepared from different mixtures, as can be seen from the data in Table 6.

TABLE 6

Date	Tensile strength (Mean kg. per sq. cm. for 10 tests)
Nov. 14	405
Nov. 23	375
Dec. 9	396
Feb. 17	393

It should be noted that these results were not obtained with identical operating techniques, for improvements were made in the technique during the period in question, and it would be expected that the reproducibility from one mixing to another would be still more satisfactory, in as much as the method now employed restricts to a still greater degree the influence of the factors which cause variable results. In any case the results fall within the range of deviations as determined above.

*Results obtained with diluted latex.*—In tests on the plantation, it is necessary to operate with latex of 35–40 per cent concentration. A simple way is to cream the latex and then to test the cream, which may easily be obtained in nearly 60 per cent concentration. However, this creaming operation eliminates soluble substances in the serum, and it would be well to know what effects these products have on the properties of the final vulcanized rubber. The attempt was therefore made to apply the technique described above directly to mixtures prepared from latex which had not been concentrated. Under these conditions the thickness of the film obtained from a single dipping was 0.005 mm. Although such a film dries fairly rapidly, it has the disadvantage that it cannot be rolled up. It was attempted to increase the thickness of the

film by enough repeated dippings to obtain a film similar to that obtained from concentrated latex. However, when operating in this way, the resulting film could not be rolled up correctly. It was next attempted to use a single dipping operation and to increase the viscosity by the addition of a suitable thickening agent. Satisfactory results were obtained with the product sold commercially before the War under the trade name of Latekoll<sup>8</sup>. The dipping bath was prepared as for concentrated latex by adding to the latex the required amounts of zinc oxide and sulfur dispersions and a solution of the accelerator so as to have a mixture of the same composition as before on the form. In addition, 3 parts of Latekoll per 100 parts of latex were added to the mixture.

From tests obtained with thirty rings, the following facts are evident. The mean value  $M$  of the tensile strength was 397 kg. per sq. cm., *i.e.*, of almost the same magnitude as the mean value obtained with concentrated latex. These two latices did not have the same origin; however, it should be borne in mind that the thickening does not have any adverse effect on the mechanical properties of the final film. Table 7 shows the values obtained for the various parameters already discussed in connection with the study of concentrated latex.

TABLE 7

Parameter	Tensile strength (kg. per sq. cm.)	Modulus at 700 per cent elongation (kg. per sq. cm.)
$M$	397	182
$\sigma$	27	11.5
$2.575\sigma$	69.5	29.5
$m$	5.4	2.3
$2.575\sigma_m$	13.95	5.1
10	9	3.8
$2.575\sigma_{10}$	23.17	9.7

The data in Table 7 show that, with respect to tensile strength: (1) the mean value is 397 kg. per sq. cm., (2) 99 per cent of the results lie between 327.5 and 466.5 kg. per sq. cm.; and (3) the true mean value of ten tests has 99 chances out of 100 of lying between 373.9 and 420.1 kg. per sq. cm.

With respect to modulus: (1) the mean value is 182 kg. per sq. cm.; (2) 99 per cent of the results lie between 153 and 212 kg. per sq. cm.; and (3) the true mean value of ten tests has 99 chances out of 100 of lying between 173 and 192 kg. per sq. cm.

The limits between which the true mean values are susceptible of varying in ten tests are 11 per cent for both the tensile strength and the modulus. These values are fairly close to those obtained with concentrated latex, but it should be noted that they were obtained with a smaller number of tests.

### CONCLUSIONS

With the method which has been described, it is possible to obtain reproducible results easily. It is hoped that the method will make it easier to study the properties of rubber mixtures prepared from latex. Furthermore the quantity of a latex mixture needed for such a test is small, *i.e.*, of the order of 400 cc., so the method is particularly well adapted to the selection of Hevea trees on a basis of the quality of their latex. As a matter of fact, it will be easy in many cases to follow the collection of latex from a limited number of trees. It should even be possible, by using a single dipping form and reducing the size of the dipping tank, to follow the quality of the latex from the daily production of one tree, a procedure which is impossible with coagulated rubber.

## ACKNOWLEDGMENT

The author wishes to express his gratitude to the Institut Français du Caoutchouc, where facilities were available for carrying out the work, and to P. Compagnon, who supervised the investigation.

## REFERENCES

- <sup>1</sup> Minatoya and Iguti, *J. Soc. Rubber Ind. Japan* **11**, 173 (1938); *India-Rubber J.* **95**, 794 (1938).
- <sup>2</sup> Chalmeau, private communication.
- <sup>3</sup> Flint, *Rev. gén. caoutchouc* **20**, 79 (1943).
- <sup>4</sup> Accelerator no. 1500 of the Rhône-Poulenc was used.
- <sup>5</sup> Distabex-L is a stabilizing agent of the Société Matières Colorantes de St.-Denis.
- <sup>6</sup> The curves in Figures 5, 6 and 7 were constructed from the means of twenty breaks.
- <sup>7</sup> Fisher, "Statistical Methods for Research Workers", 1936.
- <sup>8</sup> It is possible that this particular agent is no longer on the market, but doubtless a product of similar behavior can be found among the new thickening agents which have appeared on the market.

## OVEN AND BOMB AGING OF GR-S AT CORRESPONDING TEMPERATURES \*

J. REID SHELTON AND HUGH WINN

CASE SCHOOL OF APPLIED SCIENCE, CLEVELAND, OHIO

Attempts to correlate oxygen bomb and air oven aging generally prove unsatisfactory, particularly with GR-S. Actually, a direct correlation should not be expected since a simultaneous change in temperature and oxygen concentration is involved when they are compared under the conventional conditions for each test. The effect of temperature and of oxygen concentration have been separately evaluated by comparing the results of both oven and bomb aging at 80° and 100° C. Increased temperature was found to increase the rate of deterioration in both types of aging, but the effect appears to be more marked in the oxygen bomb. Reaction of oxygen with GR-S, which results in hardening (cross linking), appears to be virtually independent of oxygen concentration above that in air and is the predominant reaction in the air oven. Reaction of oxygen with GR-S which leads to chain scission is increased by oxygen concentration and is the predominant reaction in the oxygen bomb. Chain scission is reflected in both tensile breakdown and in a lower modulus than would otherwise be obtained since the shortening of the chains would have a softening effect; this accounts for the smaller modulus increase observed with bomb aging and for the reversion of the modulus observed at 100° C.

Attempts to correlate the aging characteristics of natural rubber vulcanizates when subjected to standard methods of accelerated aging have generally proved unsuccessful, particularly when the samples differed appreciably in compounding formulations. Neal and Ottenhoff<sup>1</sup> compared the resistance of GR-S vulcanizates to the oxygen pressure, air oven, and air pressure heat tests. They reported a complete lack of any correlation of these tests with GR-S, as previously observed with natural rubber. The oxygen bomb at 70° C and 300 pounds per square inch appeared to be the mildest, followed by the air oven at 121° C; the air bomb at 127° C and 80 pounds was the most severe.

The absence of a direct correlation between the various methods of accelerated aging is not unexpected, in view of the simultaneous change of temperature and oxygen concentration. The authors previously established that both tensile breakdown and the modulus increase brought about by aging of GR-S vulcanizates is primarily the result of attack by oxygen<sup>2</sup>, and also demonstrated the effect of temperature in the oxidation reaction<sup>3</sup>. It appeared desirable, therefore, to study the effect of temperature and of oxygen concentration independently in an attempt to explain the difference in the results obtained in the oxygen bomb and the air oven. For this purpose both types of aging were investigated at the same temperatures—namely, 80° and 100° C.

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 39, No. 9, pages 1133-1136, September 1947. This paper was presented before the Division of Rubber Chemistry at the 110th Meeting of the American Chemical Society, Chicago, September 10-13, 1946.

## PROCEDURE

A tread type of stock was employed containing the following parts by weight:

GR-S	100.0	Zinc oxide	5.0
Bardol (softener)	5.0	Santocure (accelerator)	1.2
Fat acid	1.5	Sulfur	2.0
Channel black	50.0		

All samples were cured 50 minutes at 298° F. Rectangular samples cut from tensile sheets were aged in the oxygen bomb at 300 pounds per square inch at both 80° and 100° C, and also in the air oven at the same temperatures. The air oven was of the forced circulation type, and was operated so that the maximum amount of fresh air was introduced. Triplicate samples were removed after 1, 2, 4, 6, 8, and 10 days at 80° C, and at daily intervals up to 5 days at 100° C. Tensile strips were cut from the aged samples for testing. This procedure was employed to avoid the possibility of more extensive deterioration along the edges of tensile strips cut before aging. However, comparison of the results with a duplicate set of samples aged at 100° C in the form of tensile strips showed that this precaution was not essential (Table II). The tensile strength, elongation at break, and the stress at both 200 and 300 per cent elongation were determined. The values reported in the graphs represent the average obtained with three test strips for the data at 80° C; the data presented for 100° C are the average of two independent determinations, each involving triplicate samples. The actual test data are recorded in Tables I and II.

TABLE I  
COMPARISON OF OVEN AND BOMB AGING AT 80° C\*

Method	Days aged	Tensile strength (lb. per sq. in.)	Stress (lb. per sq. in.)		Ultimate elongation (%)
			200%	300%	
.....	0	3290	760	1330	590
Oxygen bomb	1	2970	970	1670	500
	2	2930	1090	1770	480
	4	2770	1110	1800	475
	6	2680	1240	1900	440
	8	2520	1200	1820	440
	10	2300	1220	1830	410
Air oven	1	3200	1010	1740	490
	2	3220	1110	1980	450
	4	3190	1320	2170	420
	6	3140	1450	2400	380
	8	2940	1560	2490	350
	10	3020	1700	2690	345

\* Samples were aged in rectangular strips, and test strips were cut out after aging.

## COMPARISON OF AGING DATA

Figure 1 shows the change in ultimate elongation brought about by heating GR-S vulcanizate at 80° and at 100° C in both the air oven and oxygen bomb. At the lower temperature the oven is the more severe, but at the higher temperature the oxygen pressure test produces a greater change after the first day. The temperature coefficients per 10° C from the data of Figure 1 are 2.09 for the air oven and 2.63 for the oxygen bomb. Thus the effect of temperature on the rate of change in ultimate elongation is greater at the higher oxygen

TABLE II  
COMPARISON OF OVEN AND BOMB AGING AT 100° C

Method	Run no.*	Days aged	Tensile strength (lb. per sq. in.)	Stress (lb. per sq. in.)		Ultimate elongation (%)
				200%	300%	
.....	..	0	3220	740	1250	625
Oxygen bomb	1	1	2370	1080	1610	475
	2	1	2420	1070	1590	480
	1	2	1570	970	1370	380
	2	2	1530	1010	1400	350
	1	3	1330	1130	..	260
	2	3	1380	1140	..	270
	1	4	1340	1310	..	215
	1	5	1350	..	..	150
	2	5	1300	..	..	140
Air oven	1	1	3150	1400	2290	410
	2	1	3160	1350	2310	410
	1	2	3000	1610	2600	350
	2	2	3070	1600	2590	360
	1	3	3000	1760	2790	330
	2	3	2800	1790	2790	300
	1	5	2880	2010	..	275
	2	5	2860	2060	..	275

\* Runs 1, aged in rectangular strips; test strips cut out after aging. Runs 2, aged as test strips.

concentration. Considered together with the effect on tensile strength and modulus as described below, the more rapid decrease in ultimate elongation produced by oxygen pressure aging at 100° C may be attributed to an increased rate of chain scission.

The effect of aging on the tensile strength of a GR-S tread stock is much less drastic in the air oven than in the oxygen bomb, as Figure 2 shows. In fact, the decrease in tensile strength was greater at 80° C and 300 pounds per square inch oxygen pressure than in air at 100° C. Since the decrease in tensile strength may be regarded as primarily the result of chain scission, it follows

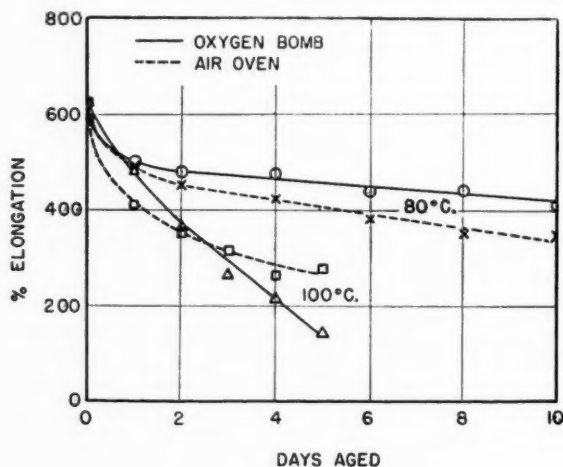


FIG. 1.—Elongation at break.



that the rate of the chain-scission reaction increases with both oxygen concentration and with temperature. The temperature coefficients per 10° C increase in temperature, calculated from the data of Figure 2 for tensile breakdown, are 1.97 for the air oven and 3.09 for the oxygen bomb.

The effect of oven and oxygen bomb aging on the stress required to produce a given elongation is shown in Figure 3 for 80° C and in Figure 4 for 100° C.

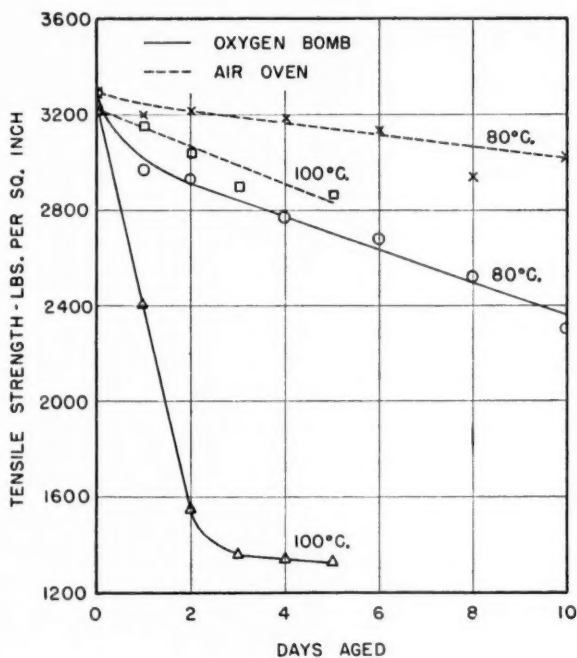


FIG. 2.—Tensile strength.

The air oven is much more drastic than the oxygen bomb in producing hardening as measured by modulus increase. At 80° C the increase in both the 200 and 300 per cent stress was about the same in oven and bomb during the first day. Thereafter the increase continued in air but leveled off at approximately a constant value in the bomb.

The authors showed previously<sup>2</sup> that the increased modulus brought about by aging in the air oven is largely the result of attack by oxygen. Since the increase is actually less in the oxygen bomb at the same temperature, it appears that this reaction is little affected by oxygen concentration above that in air and that the smaller modulus increase is due to the effect of the chain-scission reaction which tends to offset the hardening reaction. The net effect in the oxygen bomb at 80° C is a balance between the oxygen-induced hardening (which may be presumed to involve cross-linking) and the oxidative scission of chains which would have a softening effect.

This interpretation of the results is supported by the behavior of the modulus curve at 100° C, as Figure 4 shows. The stress at both 200 and 300 per cent elongation increased in both bomb and oven during the first day. During the

second day the modulus continued to increase in the air oven, although at a slower rate. The drastic reduction in tensile strength in the bomb, however, continued through the second day, with the result that the chain-scission reaction predominated over the hardening reaction and the net effect on the modulus was a decrease. Thereafter the tensile curve for the bomb aging leveled off while the hardening reaction, as measured in the oven, continued and the 200 per cent stress once more started to increase in the oxygen bomb. The slope of the curve from this point (second to fourth day of aging) is essentially the same as that of the corresponding curve for the stress at 200 per cent elongation in the oven. Since the effect of chain scission was small during this period, as shown by the tensile curves, this slope represents primarily the hardening

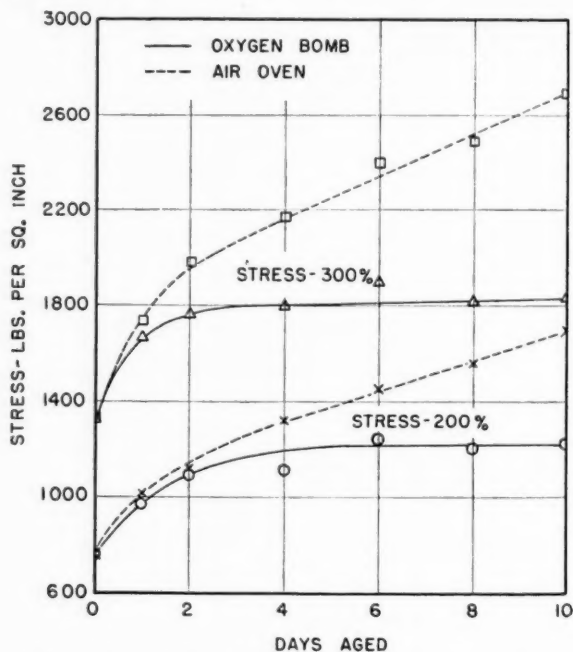


FIG. 3.—Stress at 200 and 300% elongation after aging at 80° C.

reaction and demonstrates that it is virtually independent of oxygen concentration above that in air. It was not possible to observe a similar increase in the curve for the 300 per cent stress, since the ultimate elongation was reduced below 300 per cent after 3 days in the bomb at 100° C. The shape of the modulus curves of Figure 4 and the crossover of the elongation curves at 100° C in Figure 1 show that a comparison of the effectiveness of the two types of aging cannot safely be made with a single aging period, since the relative magnitude of the changes taking place varies as aging progresses.

A reversion of the modulus (Figure 4) is quite common with natural rubber but has not been previously reported with GR-S. At first we were inclined merely to regard the data as erratic, and consequently the aging tests were repeated at 100° C. The two sets of experimental points plotted for both the 200 and 300 per cent stress in Figure 4 represent the two independent sets of

aging data, and the good agreement clearly shows that the reversion is real and the data are reproducible.

This evidence that reversion of the modulus takes place with GR-S on aging at the appropriate temperature and oxygen concentration lends support to the idea previously suggested<sup>3</sup> that the fundamental reactions involved in the deterioration of both natural rubber and GR-S are the same. These fundamental reactions appear to be (1) chain scission, which results in tensile breakdown and a reduction of stress at a given elongation, and (2) cross-linking,

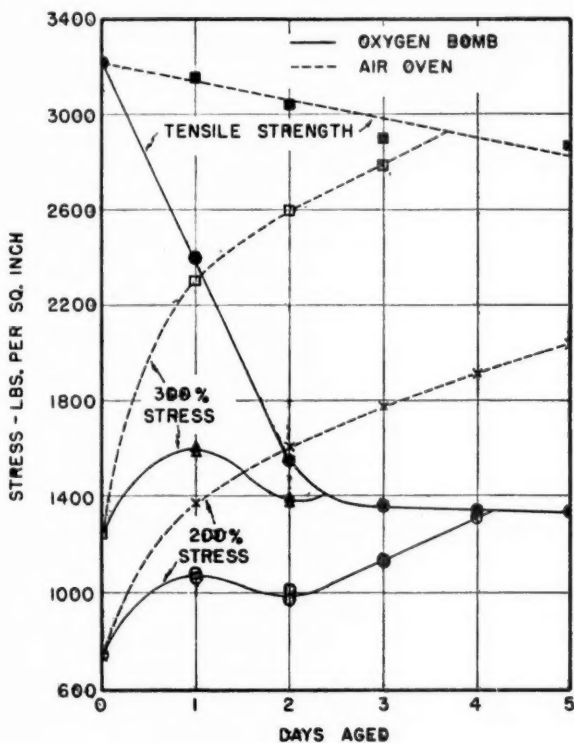


FIG. 4.—Stress at 200 and 300% elongation after aging at 100° C.

which increases the modulus and produces a general hardening. The difference between the behavior of natural rubber and GR-S under a given set of aging conditions may then be attributed to a difference in the relative rates of these two reactions. Likewise the failure to demonstrate a real correlation between the various standard methods of aging appears to be due to the fact that changes in temperature and oxygen concentration alter the ratio of these two reactions and thus change the resultant effect as measured by physical properties.

The temperature coefficient for modulus increase in the air oven, calculated from the time required to produce a given change as shown in Figures 3 and 4, is 2.00 for both the 200 and 300 per cent stress. Coefficients for bomb aging would be meaningless in this case as a result of the reversion which oc-

cured at 100° C. Harrison and Cole<sup>4</sup> determined the temperature coefficients for oven aging of GR-S over the range 100° to 132° C. Their values are compared in the following table with those obtained in the present study over the range 80° to 100° C:

Physical property	Temperature coefficient per 10° C		
	Air oven 80-100° C	Air oven 100-132° C	Oxygen bomb 80-100° C
Stress (200%)	2.00	1.97	∴
Stress (300%)	2.00	2.00	∴
Tensile strength	1.97	1.95	3.09
Elongation at break	2.09	1.96	2.63

The agreement is sufficiently close to justify extension of the relations which they establish to include the lower temperature range.

The higher temperature coefficients for both tensile strength and elongation at break, as observed with oxygen-bomb aging, may be attributed to the effect of increased oxygen concentration on the chain-scission reaction, since the cross-linking reaction appears to be little affected by oxygen concentration above that in air. The resultant effect on tensile strength is greater than on ultimate elongation, as would be expected from consideration of a typical stress-strain curve, since the elongation changes more slowly as the stress approaches the breaking load.

The evidence presented in this paper that the chain-scission reaction increases with oxygen concentration, whereas the cross-linking reaction is virtually independent of oxygen concentration above that in air, suggests certain possibilities with respect to the mechanisms of these reactions. For example, it may be postulated that, whereas both reactions are apparently initiated by oxygen, the subsequent reactions resulting in chain scission may require additional oxygen; this is indicated by the dependence of tensile breakdown on oxygen concentration, whereas the cross-linking reaction may not require any additional oxygen. The effect of oxygen concentration on the temperature coefficients is even more significant. The rate of the hardening reaction, as measured by stress increase in the oven, gives a temperature coefficient of about 2.0, and this value appears to be unchanged by additional oxygen concentration. On the other hand, the temperature coefficient for tensile breakdown increases with oxygen concentration, and since chain scission is shown to be the predominant reaction in the oxygen bomb, the higher value of about 3.1 may be regarded as an approximation of the temperature coefficient for the chain-scission reaction. The energy of activation calculated from this value is 29.7 kg.-cal. for the scission reaction; that of the cross-linking reaction is 18.2 kg.-cal. Apparently a sufficient number of oxygen molecules having sufficient energy at the temperatures involved are present in air to maintain the cross-linking reaction, and thus additional oxygen concentration becomes unimportant. However, there do not appear to be enough oxygen molecules in air with an energy of 29.7 kg.-cal. to support the scission reaction at its maximum rate. In this latter case the higher oxygen concentration in the bomb becomes an important factor.

#### SUMMARY AND CONCLUSIONS

The relations observed in this comparison of air oven and oxygen-bomb aging of GR-S at corresponding temperatures and the interpretations suggested by these relations may be summarized as follows:

1. Comparison of the results of tests in which some samples were aged in the form of tensile test strips while others were cut from rectangular strips after aging indicates that edge effects during aging are negligible and that the former practice is satisfactory.

2. Increased temperature increases the severity of both types of aging, but the effect is greater at the higher oxygen concentration of the bomb.

3. The hardening reaction, as measured by the increase in modulus, appears to be little affected by increased oxygen concentration above that in air and is the predominant reaction in the air oven.

4. Chain scission, as measured by decrease in tensile strength, increases with oxygen concentration and is the predominant reaction in the oxygen bomb.

5. Chain scission is also reflected in the smaller modulus increase observed with oxygen bomb aging compared to the air oven, and is responsible for the reversion of the modulus observed at 100° C and 300 pounds per square inch oxygen pressure.

6. Changes in temperature and in oxygen concentration, therefore, alter the ratio of the fundamental aging reactions of chain scission and cross-linking. Since the effect of these two reactions on physical properties is different, no direct correlation can be expected between methods of aging which differ in both temperature and oxygen concentration.

7. Activation energies calculated from the temperature coefficients observed for tensile breakdown in the oxygen bomb (29.7 kg.-cal.) and for modulus increase in the air oven (18.2 kg.-cal.) may be regarded as approximations of the activation energies required for chain scission and cross-linking, respectively. The observation has been made that the latter reaction is virtually independent of oxygen concentration above that in air, whereas the former increases with oxygen concentration. This may be interpreted as indicating that, at the temperatures involved, a relatively large number of oxygen molecules are sufficiently activated to maintain the lower energy reaction, even in air, while a much smaller number have the energy required for the scission reaction; consequently, increased oxygen concentration will be more effective in making a larger number of active molecules available for reaction in this case.

8. The greater dependence of chain scission on oxygen concentration may also be regarded as an indication that, although both reactions are apparently initiated by oxygen, the subsequent reactions leading to chain scission may require additional oxygen while the reactions resulting in cross-linking may not.

#### ACKNOWLEDGMENT

The authors wish to express thanks to The Firestone Tire and Rubber Company for sponsoring this Research Fellowship at Case School of Applied Science and for permission to publish this portion of the work. Thanks are also due O. D. Cole of Firestone and C. F. Prutton of Case for continued interest and cooperation.

#### REFERENCES

- <sup>1</sup> Neal and Ottenhoff, *Ind. Eng. Chem.* **36**, 352 (1944).
- <sup>2</sup> Shelton and Winn, *Ind. Eng. Chem.* **36**, 728 (1944); *RUBBER CHEM. TECH.* **18**, 116 (1945).
- <sup>3</sup> Shelton and Winn, *Ind. Eng. Chem.* **38**, 71 (1946).
- <sup>4</sup> Harrison and Cole, *Ind. Eng. Chem.* **36**, 720 (1944).

# METHODS OF AVERAGING PHYSICAL TEST RESULTS

## USE OF MEDIAN \*

J. M. BUIST AND O. L. DAVIES

RUBBER SERVICE LABORATORIES, DYESTUFFS DIVISION, IMPERIAL CHEMICAL INDUSTRIES, LTD.,  
HEXAGON HOUSE, BLACKLEY, MANCHESTER, ENGLAND

Different testing laboratories use different methods of averaging test results. Although testing methods have been drawn up by both the American Society for Testing Materials<sup>1</sup> and the British Standards Institution<sup>2</sup>, the vexed question of averaging has never received adequate attention. Horrobin and Davies<sup>3</sup> suggested a method of averaging tensile results, and although the method is sound statistically, it has never been adopted generally, for the standard deviation for each type of mix has to be known, and the method involves more calculation than is generally considered suitable for routine application.

The A.S.T.M. specifications for testing are normally excellent documents, but one general criticism which can be levelled at them is the poor methods of averaging results. The A.S.T.M. specification for tensile tests (D. 412-41) asks that "three specimens per sample shall be tested . . . in case the ultimate tensile strengths fail to check within 10 per cent of the highest value obtained, additional specimens shall be tested until two or more such check results are obtained". Later in this paper reasons are given why any method of averaging based on a percentage of the highest result is not acceptable.

In B.S. 903-1940<sup>2</sup> it is specified that four test-pieces shall be tested and the three highest results averaged. The following methods of averaging results are in use in the rubber industry:

- (1) Averaging all results within 10 per cent of the highest result.
- (2) Rejecting low results until the average of the remainder is within 10 per cent of the highest result.
- (3) Averaging the highest four results out of six, the highest three out of five, and the highest three out of four.

In this paper these different methods are assessed and compared with another method of averaging not normally used in the rubber industry, namely, taking the median of the results.

### EXPERIMENTAL DATA

It has been the practice in the Rubber Service Department at Blackley to prepare tensile sheets each week from a standard tread mix for both natural rubber and GR-S.

The details of the mixes used are as follows:

Natural rubber	100	—
GR-S	—	100
Zinc oxide	5	5
Stearic acid	1	3
Pine tar	3	—
Kosmobile-HM	50	47.5
Sulfur	2	3
Vulcafor-F	1.6	—
Vulcafor-MBT	—	0.85
Cures	50 and 60 min. at 141° C	

\* Reprinted from the *India-Rubber Journal*, Vol. 112, No. 13, pages 447-452, 454, April 12, 1947.



Six rings of the following dimensions, 52.6 mm. outside diameter, 44.6 mm. internal diameter, and 4 mm. thick, were cut from each sheet by means of a Goodbrand tensile machine with a rate of travel of the lower jaw of 400 mm. per minute. The results obtained are plotted in Figures 1 and 2. Only those results are given for which the tensile strength on all six rings are available.

It is clear from these diagrams that the spread of the results for GR-S is considerably greater than that for natural rubber.

Widely divergent low results and possibly an occasional divergent high result occur. Some method of rejection of divergent results is, therefore, desirable.

The frequency of these divergent results is seen more clearly in Figures 3 and 4, which represent the frequency polygons of the deviations of the individual tensile results from the median of each sample, *i.e.*, mean of two middle values. On inspection of the graph for natural rubber there is only one point which can be regarded as exceptionally high and perhaps three to five as exceptionally low.

Out of a total of twenty-six samples with  $26 \times 6 = 156$  results, this number of exceptional points is not large and, judging from these results, the problem is not a serious one, at least for natural rubber-tread mixes. It will be appreciated that the problem can be more serious with certain types of mixes where it is difficult to get a good dispersion of the compounding ingredients, *e.g.*, compounds containing reclaim.

In the case of GR-S, the distribution is much wider, and the tails at both ends are much longer and flatter, and there appears to be a slightly higher proportion of widely divergent results.

In both diagrams there is a certain amount of asymmetry, since the lower tail is definitely longer than the upper tail.

It is of interest to examine the distribution of the tensile results in greater detail. The individual tensile results on each sample were arranged in order of magnitude. The average value over all the samples of the highest result in each sample, the second highest, the third highest, etc., were then calculated and the mean intervals between the first highest and second highest, the second and third highest, etc., were derived. These are recorded in the following table.

Interval	Natural rubber	GR-S
(1)-(2)	4.5	10.7
(2)-(3)	3.0	5.3
(3)-(4)	2.2	8.6
(4)-(5)	3.2	11.4
(5)-(6)	11.8	13.3

The mean interval between the fifth and sixth lowest observations for natural rubber is considerably larger than between first and second or any other interval. This clearly indicates the skewness in the extreme tail and the presence of abnormally low results which must reduce the precision of the mean. This is not so evident in the case of GR-S, but the mean intervals are considerably greater, due to the larger variation. In both cases, however, a much greater degree of symmetry is obtained when we omit the lowest result.

#### COMPARISON OF METHODS OF REJECTION OF "ABNORMAL" RESULTS

A method of rejection derived from a statistical basis has been given<sup>3</sup>. This is still considered the most logical method. It involves calculating the

standard deviation ( $\sigma$ ) of the tensile results within samples and rejecting all points which fall outside  $\pm 2\sigma$  of the mean. This procedure may be simplified by considering the range of the samples, *i.e.*, the difference between the highest and lowest. The difficulty is that the standard deviation,  $\sigma$ , is not the same for all types of rubbers and would have to be calculated for each type.

The procedure of rejection based on the range is derived from the following considerations.

The distribution of the range in small samples is now known precisely<sup>4</sup>. From this we deduce that ranges greater than  $4.03\sigma$  in samples of 6, occur with a frequency of 1 in 20. When the range in any given sample exceeds this value, it is probably due to an abnormal result and if in such cases we reject an extreme result (usually a low one), then in only one sample in twenty do we reject a normal result. This risk is sufficiently small for this type of test.

The factor 4.03 is appropriate only for samples of six rings. For samples of two to five rings the maximum ranges are:

No. in sample	Maximum range
2	$2.77\sigma$
3	$3.31\sigma$
4	$3.63\sigma$
5	$3.86\sigma$

If the method rejects one result, *i.e.*, the result which deviates most from the mean, which is usually obvious from inspection, repeat the procedure for samples of five using the appropriate factor for samples of five.

This we consider to be the most logical method and should be used in research programs in which a series of samples are to be compared and where it is desired to obtain estimates of all sources of testing error. The advantage of the method is that it gives a means of separating the errors arising in mixing and curing and final tests, and may be required for tests of significance in the statistical analysis of the results.

One conclusion is immediately apparent—the spread of the results for GR-S is considerably greater than that for natural rubber. Measured as a percentage of mean tensile, the difference in spread is even greater. It is clear, therefore, that any method of rejection of low results which is based on a percentage deviation or deviation in actual magnitude from the highest or from the mean or any other value is unacceptable unless different percentages, calculated statistically, are specified for various kinds of rubbers and mixes. This would render the method quite too cumbersome for routine use. Quite apart from serious logical objections<sup>5</sup>, the above reason alone rules out the following methods:

- (a) averaging all results within 10 per cent of the highest.
- (b) rejecting low results until the average of the remainder is within 10 per cent of the highest.

It was hoped that, as a result of examination of the data on repeat identical mixes, we would obtain a clear cut comparison of the accuracy of the various methods of rejection. The criterion was to be the method which gave the smallest variation between the repeat mixes. However, it is clear from inspection of Figures 1 and 2 that there are large significant variations in tensile strength from week to week, and so the above criterion would not serve to select the best method. Since there are these significant variations, we could equally well argue that the best method is the one which discriminates best

between the samples. Clearly from their very nature, some methods of rejecting low results tend to give a "mean" on a higher or lower level than other methods. This is referred to as a bias, and provided this is present to an equal extent in all samples and all laboratories, such a bias does not matter. Apart from this bias, it was found that the differences in the results by the various

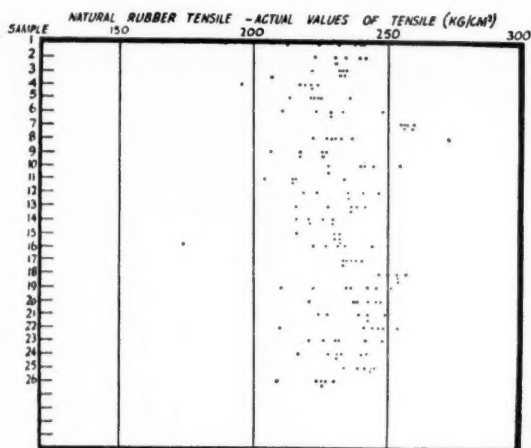


FIG. 1.

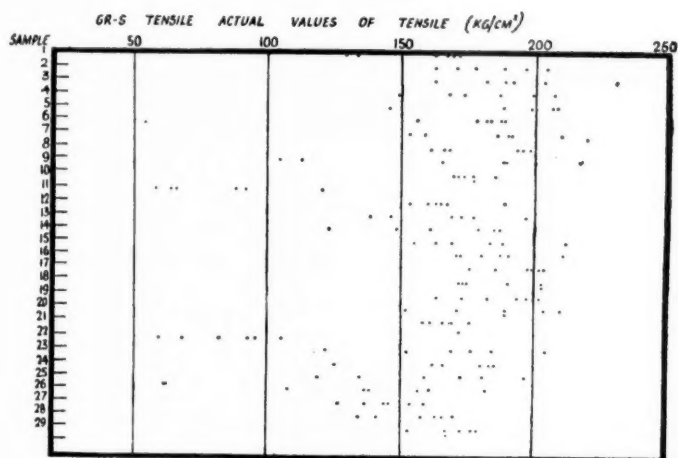


FIG. 2.

methods of "averaging" tensile tests for each sample were small compared with the variations between samples, even when we exclude the more divergent ones. In statistical terms this would mean that the interaction between samples and methods was small compared with the variation between samples. There is, therefore, little to choose in precision between the various methods of rejection, *i.e.*, between the methods:

- (1) Mean results and reject points which deviate by more than  $\pm 2\sigma$  from the mean, or reject lowest (and sometimes highest) point when the range exceeds  $4.03\sigma$ .
- (2) Always reject lowest or lowest two results and average the remainder.
- (3) Take median by averaging the two middle values.
- (4) Average four middle values.

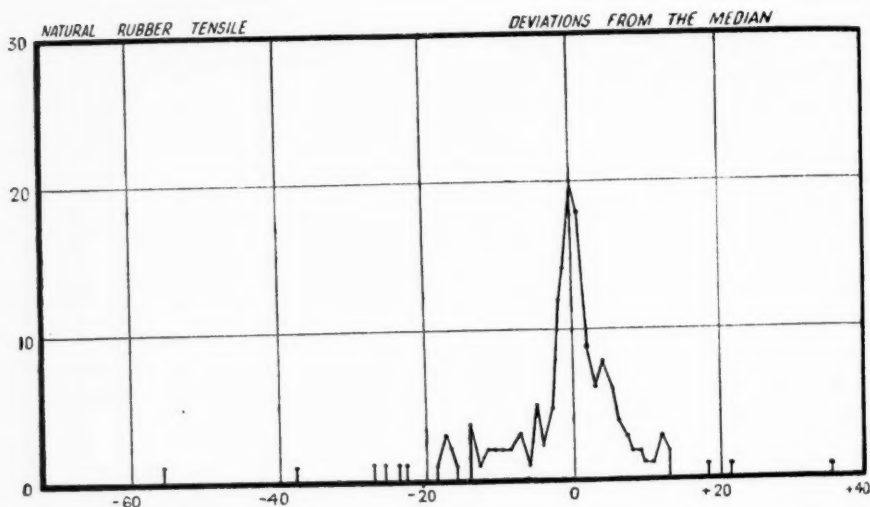


FIG. 3.

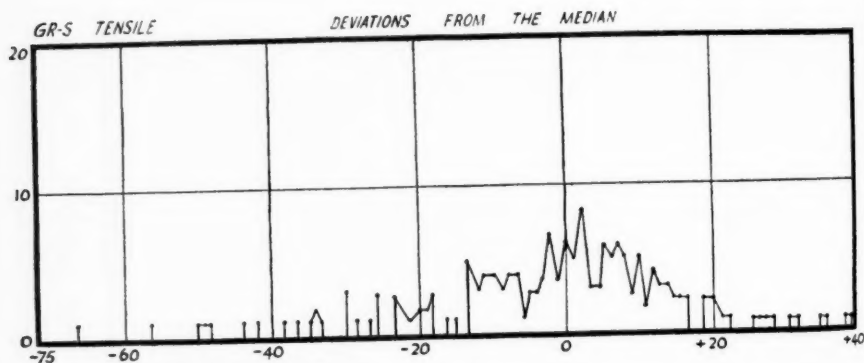


FIG. 4.

A further attempt to discriminate between the accuracy of the various methods of rejection was made as follows.

A large mix of natural rubber tread was made, sufficient to make eight tensile sheets. These were cured together. A similar mix of GR-S was made. This was repeated one week later. Smaller variations occurred between sheets cured together than between the weekly standard mixes whose results are recorded on Figures 1 and 2. But even here, no appreciable differences in

precision could be detected in the various methods of rejection, and such differences as existed were small compared with the variations between the sheets milled and cured together.

We have, therefore, to use other criteria than precision to choose between the various methods of rejection. These are simplicity, suitability for routine use and absence of bias. Method (1) is not suitable for routine use, since it tends to be complicated and involves a knowledge of  $\sigma$  which we know to vary for different types of rubber. Method (2), since it always rejects the lowest result, may introduce a slight bias. Methods (3) and (4) are both simple and free from bias, but there are cases where two abnormally low results occur and method (4) could include one of these. We conclude therefore that, from considerations of simplicity, suitability for routine use and absence of bias, method (3) is the one preferred and is the method we recommend. The choice between (3) and (4) is very slender. Either method can readily be used.

It is of interest to compare the reliability of the median and mean in samples from a normal population. It is known that the median in samples of six from a normal population is about 80 per cent as efficient as the mean. If we take the average of the middle four results, this would be almost as efficient as the mean of all six. For a skew distribution, however, the relative efficiency of the median is greater. Even if the final tensile testing were the only source of error, and even if there were no abnormal results, it is clear we do not stand to lose much in using the median in place of the mean. When we consider the other sources of error, *e.g.*, curing, milling, molding, etc., the loss in information becomes negligible. There is thus a strong case for using the median in place of the mean in almost all rubber testing, particularly in those tests with a skew distribution and tendency for abnormal high or low results to occur, *e.g.*, elongation and tear tests.

One other advantage of the median is that it is equally unaffected by an abnormal high or low result.

### SUMMARY

Different testing laboratories use different methods of averaging test results, and it would facilitate comparison of results between different establishments if a uniform procedure could be agreed upon. To facilitate the correct choice the following methods have been compared:

- (1) Averaging all results within 10 per cent of the highest.
- (2) Averaging all results until the average is within 10 per cent of the highest.
- (3) Averaging the highest four results out of six, the highest three out of four.
- (4) Taking the median.
- (5) Method of Horrobin and Davies<sup>3</sup>.

Methods (1) and (2) are unacceptable on logical grounds, but there is little to choose between methods (3) and (4). The choice for routine use rests on simplicity of method and freedom from bias. Method (3) introduces a slight bias by always rejecting the low result and, therefore, it is recommended that the median be used either by averaging the middle two out of four results or by averaging the middle four out of six results. For five rings we take the average of the middle three and for four rings the average of the middle two.

When we are interested in estimating the variations arising at each source in rubber testing, it is preferable to use the more elaborate method (5). This is considered the most logical of all methods, but it is not suitable for routine use.

## REFERENCES

- <sup>1</sup> A.S.T.M. Specifications for Rubber Products, issued annually.
- <sup>2</sup> British Standards, B.S. 903-1940.
- <sup>3</sup> Horrobin and Davies, *Trans. Inst. Rubber Ind.* **12**, 85 (1936).
- <sup>4</sup> Pearson, *Biometrika* **32**, 301 (1941-2).
- <sup>5</sup> Horrobin and Davies, *Trans. Inst. Rubber Ind.* **12**, 92 (summary) (1936).



# CHROMATOGRAPHIC ANALYSIS OF RUBBER COMPOUNDING INGREDIENTS AND THEIR IDENTIFICATION IN VULCANIZATES \*

L. J. BELLAMY, J. H. LAWRIE, AND E. W. S. PRESS

## I

### GENERAL PRINCIPLES AND METHODS

It has been the authors' experience in the use of rubber articles or components in contact with certain Government stores, such as explosives, that some ingredient of the rubber apparently had a deleterious action and, from previous knowledge of the inert nature of the usual rubber fillers and extenders when in contact with explosives, it appeared that the effect was probably produced by the accelerators or antioxidants or their degradation products. It therefore became desirable that it should be possible to identify the substances concerned.

Methods for the analysis of natural rubber vulcanizates have been described in detail in several standard text books<sup>1</sup>, in a B.S.I. Specification<sup>2</sup> and, more recently, with special reference to synthetic rubbers, in a Services Rubber Investigations publication<sup>3</sup>. These methods all aim to give a fair indication of the type of polymer employed, the extenders, and the type and quantity of fillers, but give no indication of the nature of the organic compounding ingredients, such as accelerators and antioxidants, which are normally incorporated in rather low concentrations.

From time to time papers dealing with the identification of accelerators have been published, but as the tests described were all carried out on pure or commercially pure samples, their utility was rather restricted. One of the earliest of these papers was that of Callan and Stafford<sup>4</sup>, which, at the time of publication, was quite comprehensive and, in addition to methods of detection, gave methods of estimation. A later series of papers by Shimada<sup>5</sup> described color reactions with metallic oleates. These methods were not, however, applicable to material extracted from vulcanizates, owing, first, to contamination with other compounding ingredients and to the dark color of the extract and, secondly, to the fact that appreciable decomposition apparently occurred during vulcanization.

The consumption of the accelerators, mercaptobenzothiazole and diphenylguanidine, during vulcanization has been studied by Wistinghausen<sup>6</sup>, who employed the copper derivative and picrate, respectively, to estimate the residual accelerator after-vulcanization, but attempts to apply his methods to commercial products have not been found to be entirely reliable even when used in a purely qualitative sense.

In view of the complex nature of the extracts from most modern commercial mixings and the difficulty of effecting clean separations of the components by normal analytical means, it appeared that the application of the technique of chromatographic analysis might provide a suitable means of separating and

\* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 22, No. 6, pages 308-324, April 1947.

identifying the components of an acetone extract. The authors have only been able to trace one application of chromatography in the rubber field, this being the work of Cajelli<sup>7</sup>, Levi<sup>8</sup>, and Giera<sup>9</sup> in the separation from latex of fractions of different molecular weights, but there appears to be no record of the use of this technique in the analysis of vulcanizates.

This technique, originally introduced by Tswett in 1906, remained without due recognition until comparatively recent years, when its great utility was demonstrated in such varied fields as vitamin chemistry, dyestuff analysis, the chemistry of drying oils, etc. It is an elegant method, which frequently permits the clean quantitative separation of complex mixtures not readily resolved by other means and, furthermore, when suitable adsorbents are chosen, separations can be carried out on very small quantities without the risk of chemical change. Thus, it should be possible to split an acetone extract of a vulcanizate into its component parts and separate from each other wax, fat acids, glycerides, accelerators, antioxidants, and any decomposition products formed during vulcanization.

The field is a large one and the work which the authors have been able to do so far can be regarded only as being of a preliminary and exploratory nature. Nevertheless, as will be shown in subsequent papers, sufficient has been done to demonstrate that the possibilities indicated above are capable of realization, and that individual accelerators, antioxidants, and other components of the acetone extract of a vulcanizate can be separated from each other, and that there identification is possible under conditions where normal chemical methods fail. Moreover, it has been found in practice that the mixed chromatogram method has enabled the authors to identify some of these products when present in much lower concentrations than would be susceptible to normal chemical treatment.

In addition, it has been possible to isolate from the acetone extracts of some vulcanizates certain fractions which have every appearance of being the decomposition products of the accelerator used. These have not yet been obtained in sufficient quantity to permit their complete identification, but the mere fact of their isolation leads to the suggestion that the application of this technique to the identification of the reaction products and also to the quantitative study of the consumption of accelerators during vulcanization might well throw light on the mechanism of acceleration.

As explained above, the authors were led to follow this line of investigation by the special need for analytical methods for the study of the components of vulcanizates and, although the work is by no means complete, a small number of analyses of commercial materials have already been carried out in which the antioxidants and accelerators have been successfully identified; not only by the use of mixed chromatograms, but also, in some cases, by the isolation of the pure components themselves.

For convenience this work has been divided into several parts. The first part deals with the general principles of chromatography and the practical methods employed; the second part deals with the identification of single accelerators as pure substances, or as commercial mixtures, and the third part with the identification of accelerators in actual vulcanizates. Later papers describe the work done on the identification of antioxidants, both alone and in vulcanizates.

The principles of chromatography are now fairly generally known and excellent reviews of the subject have been published by Zechmeister and Chlouny<sup>10</sup> and by Strain<sup>11</sup>. Briefly, however, the method consists of allowing

a solution of the material under examination to percolate down a vertical column which is evenly packed with a suitable adsorbent, *e.g.*, activated alumina. In general the solute is adsorbed on the column and the solvent passes through. The solute is adsorbed in a zone, the width of which depends on the diameter of the column, on the quantity of the substances present and on their adsorption affinities, which depend on the chemical structure of the compounds in question. The chromatogram is developed by further passage of solvent, which causes the zone to move down the column, the rate of travel depending on the adsorption affinity and also on the developing power of the solvent. If, therefore, a mixture is introduced on to the column, it tends to separate into different zones, depending on the relative adsorption affinities of the components, although at first these zones will probably all overlap at the top of the column. By suitable development with selected solvents the various zones can be made to move down at different speeds until separation is effected. The column may then be extruded and cut up into the appropriate sections, or the various zones may be washed through the column into separate receivers.

In effecting such separations the nature of the adsorbent and of the solvents for development is, of course, highly critical, and the choice must be based on preliminary experiment. As the name chromatography implies, the technique was originally designed for use with colored substances, with which the development of the various zones could be readily followed, but many applications have now been made with colorless materials, using various devices to detect the zones on the column. Thus, ultraviolet light, indicators and streak reagents, preliminary reaction with a colored substance, or, failing all else, empirical cutting of the column, have been used with success.

The adsorption affinity of any substance is highly characteristic of that compound; so much so, that mixed chromatograms have come to be ranked with mixed melting points in the identification of unknown materials. Thus, the formation of a single zone from a mixture of an unknown substance with a pure material, and the observation that this zone cannot be resolved into two zones by any combination of developing solvents, is now generally accepted as proof of identity of the two materials.

#### APPARATUS AND MANIPULATION

The apparatus employed is simple in character and consists essentially of a vertical glass tube containing the adsorbent supported on cotton wool. The tube is connected through an adaptor, fitted with a side arm, to a receiving flask, and the side arm is connected through a trap of a water pump so that gentle suction can be employed.

The use of ground glass joints facilitates the interchange of receivers and, by the use of suitable adaptors, columns of various sizes can be employed with the same apparatus. This is the simplest form of the apparatus which can, of course, be modified to meet specialized requirements. Thus, for fluid chromatography we have employed the apparatus shown in Figure 1. The arrangement of taps fitted to the adaptor enables the pressure to be maintained on the column while it is released in the receiver, which can then be changed. The principles of operation of this apparatus are essentially similar to those of the Perkin triangle which is used in vacuum distillation for the similar purpose of removing various fractions without interrupting the distillation. The use of a graduated receiver enables the volume of solvents passing to be measured, as this is frequently of value in the separation of colorless substances.

**Adsorbents.**—Many different adsorbents such as sugar, carbon, alumina, fuller's earth, silica gel, sodium carbonate chalk, calcium hydroxide, have been used by different workers; the choice depends on which materials give the most efficient separation of the components without decomposition. Of these materials those of widest general application are activated alumina and silica gel. So far the work has been carried out with "B.D.H. activated alumina for chromatographic adsorption analysis," and this has been found to be excellent for general separations, identification of accelerators, etc. However, this adsorbent has certain limitations, and it is proposed at a later stage to investigate more fully the use of other adsorbents, particularly silica gel, which may prove to be more suitable for certain separations.

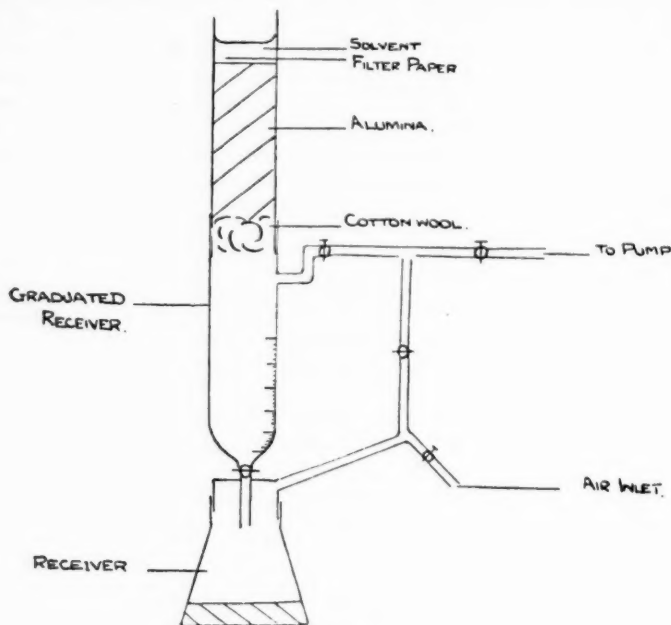


FIG. 1

**Solvents.**—It is a general rule in chromatography that materials are more strongly adsorbed from nonpolar than from polar solvents, and it is therefore usual to add the material to the column in either benzene or petroleum ether solution. The column can then be developed either with these solvents, or with benzene containing increasing amounts of polar solvents, such as alcohol or aqueous alcohol, acetone or ether, all of which are strong eluting agents. As far as rubber compounding ingredients are concerned, it was found that benzene is generally suitable for the introduction of the material on to the column, subsequent development being made with benzene, 1-alcohol-99-benzene, 5-alcohol-95-benzene, and absolute alcohol as necessary.

**Packing of columns.**—Alumina columns can be packed easily by forming a slurry of alumina in benzene and swirling until it is free from air bubbles. The slurry is then poured quickly into the column, the bottom of which is filled with a cotton wool plug. The slurry is allowed to settle under gravity and is

topped up with benzene as necessary, care being taken not to disturb the top of the column. Suction is then applied very slowly and evenly, and adjusted to a rate which will give a reasonable rate of percolation. A filter paper disc is placed on the top of the column, which is then ready for use. Once prepared the top of the column is, of course, never allowed to become dry until the operation is complete.

The packing is a most important part of the operations as careless packing results in wavy zones or in "channelling" or "coning". Nevertheless, with a little practice, it is easy to prepare good columns with alumina.

*Reverse chromatograms.*—The technique of reverse chromatograms, whereby alumina is allowed to fall slowly down a column of liquid, has received much less attention from research workers, but it was found that it can provide a rapid means of separation of certain readily adsorbed materials without the necessity of preparing packed columns. Thus, as will be shown later, almost all the common components of the acetone extract of a vulcanizate are adsorbed from benzene solution to a greater or lesser extent by alumina, with the exception of paraffin wax and mineral oil. The addition of chromatographic alumina to the benzene solution of such an extract should therefore permit of the isolation of these latter components in a relatively pure state by simple filtration, and preliminary experiments have shown this to be the case. Furthermore, by the controlled elution of the filtered alumina with selected solvents it has been found possible to obtain fractions similar to those which would be washed through a solid column by the same solvent. The eluted fractions are not always so pure and elution is probably not as complete as with the solid column, but at least this method allows of a preliminary separation of those components of particular interest, before the main chromatogram.

#### BEHAVIOR ON THE COLUMN OF COMPONENTS OF A VULCANIZATE OTHER THAN ANTIOXIDANTS AND ACCELERATORS

Before proceeding to a study of accelerators and antioxidants, either alone or in the vulcanizate, it was thought desirable to examine a few of the more common possible components of acetone extracts of vulcanizates to determine their degree of adsorption on an alumina column, not only from the point of view of their identification and analysis, but also to determine whether or not they are likely to interfere with the clean separation of the accelerator and antioxidant.

The first materials tested were paraffin wax and mineral oil, and as would be expected from their inert nature and relative freedom from unsaturation, they were found to show little or no adsorption from benzene on to alumina, and they passed straight through on development with petroleum ether or benzene. In this, as will be shown later, they differ from the other main classes of compounding ingredients, which are all adsorbed to a greater or lesser extent, and they can therefore be readily separated from them. A preliminary separation of these materials can also be effected by simple shaking with alumina in benzene solution, whereby the other components are adsorbed. The method does not make possible the separation of paraffin wax from mineral oil, but where only one of these components is present, it can be obtained in a pure state, free from other components of the vulcanizate.

Fat acid was also studied as another likely component, and was found to be strongly adsorbed on alumina, from which it would not be eluted with normal solvents, such as absolute alcohol, alcohol-water mixtures, ether, etc.



However, it could be eluted with dilute alcoholic potash and the fat acid recovered from the eluate by acidification and extraction. In this way fat acid can be separated from other ingredients of the acetone extract, which are either eluted with other eluents or alternatively resist elution with alcoholic potash. Stearic acid has been successfully isolated in this way from vulcanizates, and its determined melting point shown to be in close agreement with that of the original sample used in compounding.

Pine tar is a relatively common ingredient of many vulcanizates, and its presence is easily recognized by its odor. It was thought desirable, however, to examine the chromatographic behavior of this material, not so much from the point of view of identification, but rather to ensure that no undesirable masking effects were produced on the column when this ingredient was present in the mix. The great bulk of the pine tar was found to be strongly adsorbed as a brown-black band at the top of the column, and only one small yellow zone could be eluted from this with benzene. The rate of elution was very slow, but could be progressively accelerated with 1-alcohol-99-benzene and with 5-alcohol-95-benzene. The remainder could not be eluted with these mixtures or even with absolute alcohol so that it is unlikely to interfere with the separation of other ingredients. The brown-black zone could be eluted with acetone, and it is possible that when more samples have been examined this property may be of value as a means of isolation and identification of pine tar.

## II

### IDENTIFICATION OF ACCELERATORS

*Identification of accelerators.*—Before proceeding to a chromatographic study of accelerators themselves, a preliminary investigation was made into their color reactions with a view to their identification on the column, and also to the preparation of colored derivatives which might be chromatographed directly. A large number of papers has been published from time to time giving color reactions for the detection of accelerators, notably by Kreps<sup>12</sup>, Shimada<sup>5</sup>, Callan and Stafford<sup>13</sup> and Turk and Reed<sup>14</sup>. Of these the most promising appear to be the cobalt oleate reaction products examined by Shimada<sup>5</sup> and the copper butyl phthalate complexes described by Turk and Reed<sup>14</sup>. Nevertheless, many accelerators give the same or similar colors with these reagents, and it was therefore decided to examine the color reactions of a range of metallic oleates before proceeding further. The results obtained are given in Table 1 below and it will be seen that, apart from the lead oleate test for mercaptobenzothiazole (M.B.T.), which is fairly specific, none of them has the wide range of utility of cobalt oleate.

Metallic oleates can be conveniently prepared in the laboratory by the addition of a solution of the metallic chloride in alcohol to a benzene solution of triethanolamine oleate. Triethanolamine hydrochloride is precipitated and filtered off, leaving a solution of the required oleate. This can then be washed and purified without the emulsification difficulties which commonly arise when using the conventional method.

In addition the authors have studied the color reactions of these accelerators with a variety of alcohol soluble metallic salts, of which basic uranyl nitrate, cobalt chloride and nickel chloride appear the most promising. The results obtained are given in Table 2 below, together with those of copper butyl phthalate, and it will be seen that with these reagents certain accelerators give color reactions not shown by the corresponding oleates.



On the basis of these results it was decided to make a chromatographic study of the five common accelerators listed, together with their colored reaction products, with cobalt oleate, cobalt chloride, uranyl nitrate and copper butyl phthalate.

TABLE 1

Reagent (Solution in benzene)	Tetramethyl- thiuram disulfide (T.M.T.)	Mercaptobenzo- thiazole (M.B.T.)	Zinc diethyl dithiocarbonate (Z.D.C.)	Diphenyl- guanidine (D.P.G.)	Dibenzo- thiazyl disulfide (M.B.T.S.)
Copper oleate	Yellow-green develops on standing	Yellow ppt.	Yellow-brown	Nil	Nil
Cobalt oleate	Nil	Deep green	Very strong green	Deep purple	Nil
Nickel oleate	Nil	Red brown	Yellow-green	Nil	Nil
Lead oleate	Nil	Yellow ppt.	Yellow-green	Nil	Nil
Uranium oleate	Nil	Yellow ppt.	Orange-yellow	Pale yellow	Nil
Ferric oleate	Nil	Yellow ppt.	Red-brown	Pale yellow	Nil

Manganese, chromium and mercuric oleates gave no coloration.

The failure of M.B.T.S. to give any characteristic reactions is, of course, overcome by its reduction to M.B.T., whereby characteristic colors are obtained. In any case, as will be shown in a later paper, this reduction appears actually to occur during vulcanization, so that M.B.T. can be detected in a vulcanizate prepared with M.B.T.S.

TABLE 2

Reagent (In alcohol- benzene solution)	T.M.T.	M.B.T.	Z.D.C.	D.P.G.	M.B.T.S.
Cobalt chloride	Deep green develops on standing	Green	Intense green	Deep blue	Nil
Uranyl nitrate	Nil	Nil	Orange- yellow	Nil	Nil
Nickel chloride	Nil	Nil	Green	Nil	Nil
Copper butyl phthalate	Brown on standing	Pale yellow	Dark brown	Nil	Nil

#### CHROMATOGRAPHY OF ACCELERATORS

The behavior of single common accelerators when chromatographed on alumina was studied. T.M.T., Z.D.C., M.B.T., M.B.T.S. and D.P.G. were all well adsorbed on alumina with benzene solution, and could not be eluted by repeated washing with this solvent. All of them could, however, be eluted at varying rates with 5-alcohol-95-benzene, although the elution of M.B.T. was slow, and was completed with absolute alcohol. Attempts to differentiate the various zones by viewing in ultraviolet light were disappointing, none of the compounds studied showing any characteristic fluorescence. The strong apparent fluorescence of M.B.T.S. has been traced to the presence of very small quantities of an impurity which is separated by this method.

Nevertheless, evidence has been obtained by empirical methods that these compounds do separate into individual zones, and the authors have been able to separate a mixture of T.M.T. and D.P.G. in this way. However, in view of the laborious nature of empirical cutting of the column, it was decided to

concentrate on the chromatography of the color reaction products of accelerators. In all cases typical commercial materials were used as being those likely to be encountered in practice, but recrystallized materials were also examined in an attempt to differentiate zones due to impurities from those given by the accelerator itself.

*Chromatography of accelerator solutions containing cobalt oleate.*—An excess of a 10 per cent solution of cobalt oleate in benzene was added to a benzene solution of the accelerator but, in general, the color of the accelerator complex (see Table 1) was marked or modified by that of the excess cobalt oleate. When the solution was added to the alumina column, the cobalt oleate itself was strongly adsorbed at the top of the column as a pink zone, which previous experience has shown could not be eluted even with aqueous alcohol. All colored zones other than this can, therefore, be safely regarded as being derived from the accelerators. In some cases a series of colored zones was obtained, indicating that the accelerators were not pure chemical individuals, but as the same series of zones was obtained using recrystallized material, it is probable that they are closely related individuals and that the number and color of the zones are characteristic of the accelerators, at least in so far as experience on materials from a number of different sources is concerned.

The chromatographic results obtained are given at Table 3 below. In the consideration of the results it should be borne in mind that development is proceeding all the time, the development of zones being a matter of relative speeds. Whereas, therefore, one operator might report a zone as developing rapidly with 5-alcohol-95-benzene, another might report it as developing very slowly with 1-alcohol-99-benzene. Nevertheless, the chromatograms are sufficiently characteristic to be identifiable, especially if the mixed chromatogram technique is employed. The method enables the various greens produced with different accelerators to be differentiated. Thus, although the results are not reported fully here, the authors have examined, in addition to Z.D.C., sodium diethyldithiocarbamate, piperdinium pentamethylenedithiocarbamate, and a proprietary thiocarbamate accelerator. Each of these gave a green color with cobalt oleate which is resolved on the column to a characteristic chromatogram.

*Chromatography of accelerator solutions containing uranyl nitrate.*—Of the accelerators so far studied, uranyl nitrate appears to react only with the dithiocarbamates, giving intense blood-red, orange or yellow colors. In the case of Z.D.C., an orange-yellow solution is obtained which is firmly adsorbed by alumina to give a lemon-yellow zone. This zone cannot be readily developed further, remaining tightly held near the top of the column beneath the excess of uranyl nitrate. This reagent should, therefore, prove valuable, not only in the identification of dithiocarbamates, but also in the separation of them from other accelerators which do not react with uranyl nitrate and can, therefore, be eluted from the column, free from Z.D.C. or other similar materials. The solution in uranyl nitrate should, however, be allowed to stand for a few hours to allow the reaction to go to completion, since with Z.D.C. the reaction is slow, and it has been possible to detect unreacted Z.D.C. in the alcohol eluate from columns prepared immediately after the addition of the uranyl nitrate.

*Chromatography of accelerator solutions and copper butyl phthalate.*—D.P.G. and M.B.T.S. give no reaction with this reagent, which may therefore be used for the detection of other accelerators mixed with them. Z.D.C. gives an immediate dark brown color as do other dithiocarbamates tested, and T.M.T. develops a similar color on standing. The yellow color developed with M.B.T.

TABLE 3  
COBALT OLEATE IN BENZENE WITH M.B.T., Z.D.C. AND D.P.G. CHROMATOGRAPHED ON ALUMINA

Accelerator	M.B.T.	Z.D.C.	D.P.G.
Initial appearance of column	Gray zone at the top	Green zone at the top	Purple-violet zone immediately below the pink of the excess cobalt oleate
Benzene development	Nil	Diffuse apple-green zone passes rapidly down the column. Yellow and green zone remain at top of the column	Nil
1-Absolute alcohol-99-benzene development	The gray ring splits into its components, the pink of cobalt oleate on top and the green due to M.B.T. below. On further washing the green complex decomposes, the color disappears, and M.B.T. passes out	Yellow zone developed slowly from the top of the column	Nil
5-Absolute alcohol-95-benzene development	Development of M.B.T. continued	Yellow zone referred to above developed rapidly	Nil
Absolute alcohol development	Nil	Brown zone developed from the top: A green zone remains at the top of the column and is not eluted	Nil. The D.P.G.-cobalt complex remains firmly held and is not eluted

In connection with these results the following points of interest arise.

(1) D.P.G., as a cobalt complex, is firmly held at the top of the column. This provides a means of identification and also a means of separating it cleanly from M.B.T., M.B.T.S. and T.M.T., all of which are eluted as such with 5-alcohol-95-benzene.

(2) The behavior of the M.B.T. complex is interesting and characteristic, in that it is the only one of the accelerator derivatives so far examined which decomposes on the column. The production of a green zone which fades with 1-alcohol-99-benzene and the subsequent redevelopment of a green color on testing the eluate with fresh cobalt oleate would appear to be characteristic for M.B.T.

(3) The initial apple-green zone given by Z.D.C., which is not adsorbed and which passes out in benzene, may be due to some impurity common to the dithiocarbamate series, as P.P.D., S.D.C. and the proprietary accelerator also give this phenomenon. However, the number and variety of the zones obtained is sufficient to characterize this material, especially if a mixed chromatogram is performed with an authentic sample.

(4) Mixtures of M.B.T. and D.P.G. have been successfully identified in this way, the M.B.T. portion being eluted with alcohol and obtained free from D.P.G. The method has also proved successful in identifying D.P.G. in a proprietary material consisting of a mixture of accelerators of which D.P.G. is one component.

is pale and unlikely to be of value for the detection of this compound in extracts from rubber.

Chromatography of the dark brown solutions obtained with the dithiocarbamates and with T.M.T. gave in all cases a very broad dark brown zone which passed straight through in benzene. Nothing further could be developed with 1-alcohol-99-benzene, but 5-alcohol-95-benzene developed a pale brown zone and absolute alcohol another similar zone. It is probable that these

TABLE 4  
COBALTOUS CHLORIDE SOLUTION WITH D.P.G., T.M.T., Z.D.C., M.B.T. AND M.B.T.S.  
IN BENZENE, CHROMATOGRAPHED ON ALUMINA

Accelerator	D.P.G.	T.M.T.	Z.D.C.	M.B.T.	M.B.T.S.
Initial color	Deep blue	Deep green on standing	Green	Green	Blue (due to excess reagent)
Appearance of chromatographic column (alumina)	Totally absorbed as blue zone at the top*	Green zone with narrow brown zone at the top	Green zone with yellow brown zone near the top	Blue zone at the top	Dark blue zone (due to excess reagent)
Benzene development	Nil	Green zone with blue leading edge passes straight out	Green diffuse zone with blue edge. Moves out. Yellow zone moves very slowly	Nil	Nil
Benzene + 1% alcohol-benzene	Nil	Nil	Yellow zone developed which coalesces with that above and moves slowly	Green zone moves slowly down and fades. Pure colorless M.B.T. developed	Nil
Benzene + 5% alcohol-benzene	Nil	Brown zone at top eluted as pale yellow zone	Nil	M.B.T. development continued	Nil
Absolute alcohol elution	Nil. No D.P.G. developed		Nil		Nil

\* Although the addition of the reagent to a solution of D.P.G. produces a definite intensification of the blue, no differentiation between the zones due to the complex and to the excess reagent could be observed on the column.

zones move at different rates with different accelerators, and a chromatogram from a mixture of the two accelerators might serve to show that such a mixture was present by their separation into two zones. On the other hand, the chromatograms are so essentially similar as to be of little value in characterizing those materials which give colored reaction products.

*Chromatography of accelerators and cobaltous chloride.*—Anhydrous cobaltous chloride was dissolved in an absolute alcohol and diluted with as great a volume of benzene as possible without causing precipitation. This was to ensure that as little alcohol as possible was present during the initial stages of the chromatogram. With the same object, the minimum excess of reagent necessary to produce a satisfactory color with the accelerator was used in all cases. As with cobalt oleate, any excess of reagent was strongly adsorbed at the top of the column, in this case as a dark blue zone, so that the colored zones developed below can be regarded as being derived from the accelerator.

#### CONCLUSION

The study of the chromatographic behavior of certain colored reaction products of T.M.T., Z.D.C., M.B.T. and D.P.G. has shown that individual materials can be clearly differentiated from each other and from similar materials of related chemical composition. Where two or more accelerators give the same color with cobalt reagents, this technique enables them to be characterized. By a study of the results obtained it is possible to devise a series of tests whereby the components of any mixture of these materials can be successfully identified.

The following scheme for the identification of D.P.G., T.M.T., Z.D.C., M.B.T. and M.B.T.S., which is applicable to any mixture of these accelerators, is suggested on this basis:

- (1) Z.D.C. removed with uranyl nitrate on a column. The remaining accelerators are eluted with 5-alcohol-95-benzene.

- (2) D.P.G. removed with cobalt oleate on a column. M.B.T. detected as a green zone, decomposing on elution with alcohol-benzene. Alcohol-benzene eluate now contains M.B.T., M.B.T.S. and T.M.T.
- (3) T.M.T. removed with cobaltous chloride and green zone washed through with benzene. M.B.T. and M.B.T.S. then eluted with 5-alcohol-95-benzene.
- (4) M.B.T. precipitated with lead oleate, filtrate chromatographed and M.B.T.S. eluted with alcohol-benzene.
- (5) Solvent removed and M.B.T.S. reduced with magnesium and sulfuric acid; the resulting M.B.T. extracted with benzene and detected as at (4).

The alcohol is removed at each stage by evaporating down with benzene.

As will be shown in the following section, this technique has been successfully applied to vulcanized rubber mixes where the identification of the accelerators is normally a much more difficult problem, partly due to the small quantities of residual accelerators present, and partly to the masking of the color reactions by waxes and other colored products present in the acetone extract.

### III

#### IDENTIFICATION OF CERTAIN ACCELERATORS IN VULCANIZATES

In the previous sections of this work the general technique of chromatography was described, together with its application to the identification of certain of the more common accelerators. This section describes the application of this work to the detection of these accelerators in a vulcanized mix. It has been possible to show that in certain cases a single chromatographic operation makes possible the clean separation of wax, or mineral oil, fat acid and accelerators from each other and, as will be shown later, from some anti-oxidants. Modifications in technique are necessary to deal with special cases, but sufficient has been done to demonstrate the possibilities of this method in the analysis of vulcanizates, and to indicate certain of the more common ingredients which can be separated in this way.

The whole of the work on accelerators in vulcanizates has been carried out on acetone extracts from which the acetone has been removed and benzene substituted as a solvent, and it has been found that the chromatograms prepared from this solution not only make possible the separation of the ingredients already quoted, but also that the portion of the acetone extract derived from the rubber can be resolved into a number of fractions. In addition, the authors have obtained indications of the presence in the vulcanizates of breakdown products of the accelerators, and these can be cleanly separated from any residual accelerator. These findings have not yet been followed up, but the method is clearly of great promise as a means of studying the chemical changes occurring during vulcanization and as a means of following the decomposition of accelerators during cure.

*Chromatographic behavior of accelerators in vulcanized mixes.*—The chromatographic behavior of accelerators alone and after reaction with cobalt oleate has already been described, and as a next step it was decided to prepare a series of natural rubber mixes containing rather large proportions of accelerators to give an opportunity to determine the relative position of the accelerators on the column in relation to other compounding ingredients.

Accordingly mixes were prepared as indicated below and vulcanized to the approximate optimum cure in each case. After sheeting, 10–20 grams was extracted with acetone, and the dried extract dissolved in benzene. As a blank test an unaccelerated mix of otherwise similar composition was prepared, and vulcanized to give both undercured and overcured samples, to determine the relative positions of other ingredients, *e.g.*, zones due to materials originating from rubber, etc. For reasons already given, the choice was limited to a few of the more common accelerators, and antioxidants were omitted from these mixes to simplify the chromatogram as much as possible.

Mix	A	B	C	D	E	F
Pale crepe	100	100	100	100	100	100
Parafin wax	1	1	1	1	1	1
Stearic acid	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5
Sulfur	8	3	3	1	1	3
Mercaptobenzothiazole (M.B.T.)	—	1	—	—	—	—
Benzothiazyl disulfide (M.B.T.S.)	—	—	1	—	—	—
Tetramethylthiuram disulfide (T.M.T.)	—	—	—	1	—	—
Zinc diethyldithiocarbamate (Z.D.C.)	—	—	—	—	1	—
Diphenylguanidine (D.P.G.)	—	—	—	—	—	1

#### CHROMATOGRAPHIC BEHAVIOR OF SOLUTIONS OF EXTRACTS FROM VULCANIZATES

*Unaccelerated vulcanizate.*—Solutions of the extracts from both the undercured and overcured vulcanizates of mix A prepared as described above gave relatively simple chromatograms on alumina. In both cases a broad yellow zone passed straight out in benzene, this being the fraction containing the wax. The yellow coloration was due to contamination with elementary sulfur, but no difficulty was experienced in obtaining the wax free from other ingredients. No further development with benzene could be obtained in either case, and both chromatograms showed a broad brown zone at the top. With 1-alcohol-99-benzene little development was observed, but in the case of the undercured mix the top zone split into two light brown zones, the lower of which moved very slowly. The rate of development of this zone was considerably accelerated with 5-alcohol-95-benzene, and with this eluent a similar zone was developed from the overcured mix. This zone was eluted and found to consist of a small quantity of material which was apparently derived from the rubber.

Nothing further appeared to be eluted with absolute alcohol, although stearic acid was subsequently eluted with alcoholic potash, as previously described. On recrystallization, stearic acid of the same melting point as that used was obtained. No other colored zones were detected in these chromatograms, and from the results obtained it was concluded that any fractions of rubber origin developed were unlikely to interfere in the separation or identification of other organic components of the mix.

*M.B.T. accelerated vulcanizate.*—A solution of the extract from Vulcanizate B, found as described, was found to give a simple chromatogram similar in appearance to that obtained from Vulcanizate A.

It has already been shown that M.B.T. is not eluted from alumina with benzene but can be readily removed with 5-alcohol-95-benzene. As a preliminary method of concentration, therefore, the wax fractions were washed out with benzene, and the M.B.T. fraction subsequently collected separately by elution with 5-alcohol-95-benzene. The extract was only slightly colored,



and the fat acid and materials derived from the rubber were firmly retained on the column. The eluate was evaporated to dryness to remove alcohol, redissolved in benzene, and a slight excess of cobalt oleate added. The solution immediately developed the characteristic green color given by M.B.T. with this reagent. The colored solution was then chromatographed, and the green material was found to be adsorbed at the top of the column immediately below the pink zone of excess cobalt oleate. On washing with benzene no further development occurred, but with 5-alcohol-95-benzene the green zone began to move down, losing color as it did so, and finally passed out of the column as a pale yellow zone. This decomposition of the cobalt complex is characteristic of M.B.T. Concentration of the eluate and recrystallization from absolute alcohol gave pure M.B.T., m.p. 174° C, which showed no depression of melting point on admixture with an authentic specimen. Furthermore, a mixed chromatogram of this recovered material with an authentic specimen in the presence of cobalt oleate gave only a single green zone, developing with 5-alcohol-95-benzene into a single yellow zone.

*M.B.T.S. vulcanizate.*—A solution of the extract from Vulcanizate C, prepared as described, gave a simple chromatogram on alumina. With benzene development two zones, one yellow and the other brown, were developed. The yellow zone which contained the wax passed out first and was separated from the second zone, which was found to be too small to permit further examination. On elution with 5-alcohol-95-benzene a further pale yellow-brown zone was developed rapidly, while a second brown zone commenced to move down slowly. The first of these zones was collected and a portion tested with cobalt oleate, whereby the characteristic green color associated with M.B.T. was observed. The alcohol was then removed from the remainder of this fraction, cobalt oleate added, and the solution chromatographed. The chromatogram obtained was identical with that described for M.B.T. above, the green zone decomposing and the eluate giving a strong green color with fresh cobalt oleate. M.B.T. was then added to the eluate, together with excess cobalt oleate, and the solution again chromatographed. The behavior on the column was identical with that previously observed, indicating that M.B.T. was present in the acetone extract of a mix in which M.B.T.S. alone had been compounded. It is therefore clear that M.B.T. is one of the reaction products formed during the vulcanization of a M.B.T.S. accelerated mix. This fact, although facilitating the identification of the general class of accelerator (M.B.T.S. itself gives no cobalt oleate reaction), must necessarily complicate any differentiation between M.B.T.S. and M.B.T.

*Z.D.C. accelerated vulcanizate.*—As in the cases reported above, a solution prepared from the acetone extract from Vulcanizate E gave a relatively simple chromatogram, consisting in this case of three brown zones at the top of the column with a yellow one below. On development with benzene the yellow zone (wax) passed out rapidly, followed more slowly by a faint reddish-pink zone. With 5-alcohol-96-benzene, two of the brown zones at the top were eluted and were collected together. A portion of this fraction gave an intense green with cobalt oleate solution. The alcohol was therefore removed from the remainder and the residue redissolved in benzene. This solution was then treated as follows:

To one portion excess cobalt oleate was added and the resulting solution chromatographed. The chromatogram gave all the zones previously described as characteristic of Z.D.C.; notably the broad unabsorbed green zone, and the green zone which cannot be eluted with absolute alcohol. The yellow zone

given by Z.D.C. which is eluted with 5-alcohol-95-benzene could not, however, be separately distinguished, as two brown-yellow zones were developed with this eluent, one of them presumably being due to some material other than Z.D.C.

To another portion an authentic specimen of Z.D.C. was added, followed by an excess of cobalt oleate, and the resulting solution was chromatographed. The chromatogram was identical with that obtained above and did not show any additional zones, thus confirming the presence of Z.D.C. in the original eluate.

*T.M.T. accelerated vulcanizate.*—The chromatogram developed from the benzene solution of the extract from Vulcanizate D was also simple, and contained only brown and yellow zones. The fraction eluted with 5-alcohol-95-benzene was separated as a light yellow zone, this being the portion in which one would expect to find the T.M.T. After removal of the alcohol the addition of cobalt oleate to a portion gave a brilliant green solution, which was chromatographed and developed with benzene. A broad green zone was eluted fairly rapidly, leaving at the top of the column a brown zone, a second brown zone and a dark green zone arranged in that order and all firmly retained. Development with 5-alcohol-95-benzene solution eluted a light brown zone and effected some slight further separation of the zones at the top. With absolute alcohol, the second brown zone developed rapidly, passing through the dark green zone which developed only very slowly. The upper green zone remained unchanged.

It will be seen that, with the exception of the lower dark green zone, the development of this chromatogram is identical with that of Z.D.C. with respect to colored zones produced by cobalt oleate, whereas it has been shown previously that T.M.T. itself gives no color with this reagent. This formation of Z.D.C. during vulcanization from a mix containing sulfur and T.M.T. is interesting and may be compared with the results obtained by Dufrasse and Jarrijon<sup>3</sup> who, on the evidence of ultraviolet adsorption measurements, showed that Z.D.C. occurs as a reaction product when T.M.T. acts as a direct vulcanizing agent. The reserved portion of the original eluate was therefore concentrated and allowed to crystallize when small needles were obtained. These were chromatographed with cobalt oleate alone and with cobalt oleate, together with an authentic specimen of Z.D.C. An identical chromatogram was obtained in each case, indicating that Z.D.C. is in fact formed during vulcanization.

The production of the second green zone is interesting, and as T.M.T. itself gives no reaction with cobalt oleate, this can be attributed only to some other breakdown product produced during vulcanization. If this can be established over a sufficiently large number of mixes, it may well provide a means of differentiating between mixes originally compounded with T.M.T. and those originally compounded with Z.D.C.

*D.P.G. accelerated vulcanizates.*—The vulcanizate containing D.P.G. differed from the others examined in that the prepared solution of the extract without addition of excess cobalt oleate gave a complex chromatogram, with many highly colored zones. In the limited series of accelerated vulcanizates examined, the formation of this complex group of colored zones appears to be characteristic of D.P.G., but sufficient work has not yet been done to determine whether other substituted guanidines give similar chromatograms.

On initial development with benzene, the colored zones were observed in the following order: yellow-brown (top), black-brown, purple, red with brown top, yellow-orange, yellow (bottom).

With further benzene development the lower zones move down and become more clearly differentiated. The bottom pale yellow zone containing the wax is eluted first, and is followed by, and clearly separated from, a narrow orange-yellow zone. This second zone was found, on removal of the solvent, to have a strong odor of carbylamine, suggesting that this is one of the decomposition products of D.P.G. The third zone is developed only slowly with benzene, but can nevertheless be washed completely out of the column. It consists of three brightly colored zones developed from the purple and red zones previously observed. The zones are narrow, brightly colored and clearly separated. A bright red zone is eluted first, followed by a brown zone and then by a purple zone. The actual amount of material present in these zones was very small.

The top two zones were not further developed with benzene, although they showed some slight resolution into further zones, including a faint green and a faint yellow zone.

With 5-alcohol-95-benzene the two top zones are resolved into a number of others as follows: brown (top), yellow-buff, brown, lemon-yellow, green (bottom). On further development the green and yellow zones move at a fair speed, and the remaining three zones show some further separation from each other. None of the fractions eluted at this stage gave a positive reaction for D.P.G. with cobalt oleate.

With absolute alcohol the yellow-buff zone was eluted slowly, leaving the top brown zone on the column. This behavior has been observed in a number of D.P.G. vulcanizates and, within the authors' limited experience, is characteristic. The red and purple zones in the first stage of the elution and the green and yellow zones in the second are suggested as the most suitable for identification purposes when considered in conjunction with the others.

#### SENSITIVITY OF THE METHOD FOR ACCELERATORS

To obtain some idea of the sensitivity of the method for the detection of accelerators in vulcanized mixes, a series of mixes was prepared in which low accelerator concentrations were used. The compositions of these mixes were as follows:

Mix	A	B	C	D	E	F
Pale crepe rubber	100	100	100	100	100	100
Paraffin wax	1	1	1	1	1	1
Stearic acid	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5
Sulfur	8	3	3	1	1	3
Mercaptobenzothiazole (M.B.T.)	—	0.1	—	—	—	—
Benzothiazyl disulfide (M.B.T.S.)	—	—	0.1	—	—	—
Tetramethylthiuram disulfide (T.M.T.)	—	—	—	0.1	—	—
Zinc diethyldithiocarbamate (Z.D.C.)	—	—	—	—	0.1	—
Diphenylguanidine (D.P.G.)	—	—	—	—	—	0.1

The mixes were all vulcanized to the approximate optimum cure and, after sheeting, 10 grams was extracted with acetone. The extract therefore corresponds to 0.01 gram of original accelerator. The extracts were prepared as before, chromatographed, and the 5-alcohol-95-benzene eluate collected. The alcohol was removed, the residue dissolved in benzene, cobalt oleate added, and the solution rechromatographed. No difficulty was experienced in detecting the characteristic multicolored series of zones given by D.P.G., and some indications were obtained of both Z.D.C. and T.M.T., but M.B.T. and

M.B.T.S. could not be detected at this concentration. Both Z.D.C. and T.M.T. appeared to be at the limit of sensitivity, since no color could be detected with certainty on the column while wet with solvent. On drying, however, the green zone of Z.D.C., resistant to elution with absolute alcohol, was clearly visible in both cases. The failure to detect M.B.T. and M.B.T.S. is not altogether surprising at this low concentration, as the color reaction of M.B.T. with cobalt oleate is less sensitive at low concentrations than with the other accelerators. With a view to obtaining some further information as to the limits within which these latter compounds could be detected a further chromatogram was run on an extract prepared from 50 grams of the vulcanizate containing M.B.T.S. This weight of vulcanizate therefore corresponds to 0.05 gram of original accelerator. After separation of the fraction eluted with 5-alcohol-95-benzene, which has been previously shown to contain the accelerator fraction, no difficulty was experienced in obtaining the characteristic vivid green color reaction given by M.B.T. with cobalt oleate. A mixed chromatogram with an authentic specimen of M.B.T. in the presence of cobalt oleate was identical with that previously obtained. It is therefore clear that, despite the relative insensitivity of the cobalt oleate reaction, this method makes possible the identification of M.B.T. or M.B.T.S. in smaller quantity than would be possible by normal chemical methods.

#### IV

#### IDENTIFICATION OF ANTIOXIDANTS

Unlike accelerators, the majority of which are either single chemical compounds or mixtures of these compounds in fixed proportions, antioxidants, with few exceptions, are complicated mixtures of closely related compounds. It would, therefore, be expected that these materials would, in general, give more complex chromatographs than those given by accelerators.

In addition, as antioxidants are not themselves characteristically colored, it would be expected that difficulty would be encountered in determining their position on the column and following their behavior under the influence of eluents. Some, but not all, antioxidants are known to fluoresce in ultraviolet light, but it appeared to be desirable to examine some reactions of these materials with a view to developing suitable reagents for their identification. As in the case of accelerators, the work on antioxidants to date has been confined to a few of those most commonly used.

*Color reactions.*—Since many antioxidants are derivatives of secondary amines, it seemed reasonable to suppose that the colors developed by various oxidizing agents might be sufficiently distinctive to permit a scheme of identification to be formulated. The oxidizing agents studied are as follows: (1) a mixture of concentrated nitric acid and sulfuric acid (1:3); (2) ammonium vanadate in concentrated sulfuric acid (1 per cent); and (3) potassium dichromate in concentrated sulfuric acid (1 per cent).

The colors obtained as spot tests on a white tile, using freshly prepared reagents, are shown in the table which follows, together with the colors obtained with concentrated sulfuric acid alone.

It will be seen that the use of any one of these reagents is inadequate for the complete identification of an individual member of the group, but this can be achieved by making use of the colors developed by each of the reagents, *e.g.*, B.L.E. gives a green color with the ammonium vanadate reagent and with the potassium dichromate reagent, but with nitric-sulfuric acid mixture it gives a

violet color, thus distinguishing it from those antioxidants which give green colors with the first two reagents.

In using these tests it has been found advantageous, more especially when several antioxidants give rather similar colors with a reagent, to confirm the identity of the antioxidant by a blank test, using an authentic specimen of the material whose presence is suspected.

Antioxidants	Sulfuric acid	1% Ammonium vanadate in sulfuric acid	1% Potassium dichromate in sulfuric acid	Nitric acid/sulfuric acid (1:3)
Phenyl- $\alpha$ -naphthylamine	Faint green	Vivid green	Green-blue	Green
Phenyl- $\beta$ -naphthylamine	Pale yellow	Very faint green-yellow	Brown-green	Red
Agerite White	Green	Prussian blue	Red, changing to Prussian blue	Purple
Flectol-H	Nil	Faint red-brown	Faint red-brown	Bright red
Agerite Stalite	Nil	Nil	Strong brown ochre	Green
B.L.E.	Nil	Green	Green	Deep violet
Nonox-S	Faint brown-green	Brown	Nil	Brown
Vulcaflex-A	Green	Dark blue-green	Dark green-blue	Crimson
Neozone H.F.	Brown-green	Emerald green	Red, changing to emerald green	Red

#### ANTIOXIDANTS ON ALUMINA COLUMNS

*General.*—With one exception the antioxidants examined are only weakly adsorbed on to alumina columns from benzene solution, and this with the absence of distinctly colored zones, renders the technique of the mixed chromatogram of doubtful applicability, except perhaps when long columns are used. Where single chemical individuals such as phenyl- $\beta$ -naphthylamine are involved, however, no difficulty is experienced in their isolation in a pure state, and their subsequent identification by the preparation of derivatives and determination of melting points. In this case the passage of the antioxidant zone through the column was followed by means of the fluorescence of phenyl- $\beta$ -naphthylamine in ultraviolet light. It should be noted, however, that whereas many antioxidants fluoresce in ultraviolet light, care must be exercised in the use of this method, as some accelerators and other compounding ingredients, *e.g.*, mineral oils, are known to fluoresce under the same conditions.

To characterize the position of antioxidants on the column with more certainty, the reagents described on the color tests above were used as streak reagents and found to be satisfactory. This technique involves the extrusion of the moist column and the application of the reagent to the extruded column by means of a fine capillary or by a glass-fiber brush, when the location of the antioxidant zone is shown by the development of color. If a sufficiently narrow streak is made on the column, the contaminated material can be readily scraped away, leaving the remainder for further examination.

It is necessary to exercise caution in the use of the vanadate reagent in the presence of benzene, since it has been found that a more concentrated solution gives a red color with benzene, and as extruded columns are usually wet with this solvent, it is important that the concentration of the ammonium vanadate should not be greater than 1 per cent.



*Behavior of individual antioxidants: Phenyl- $\alpha$ -naphthylamine.*—This material shows a brilliant violet fluorescence when viewed in ultraviolet light, and this persists in benzene solution and when adsorbed on the alumina. No difficulty was, therefore, experienced in following the behavior of this material on a chromatographic column, and it was found to be only weakly adsorbed from benzene solution. On further development with benzene, the antioxidant moved slowly down the column and was eluted quantitatively. The material eluted retained the characteristic pink color of the  $\alpha$  compound, it gave strong green-blue colorations with the spot reagents described above, and its purity was confirmed by the melting point. As a confirmatory measure to the usefulness of the vanadate reagent on alumina, a second column was prepared and developed in the same way and extruded while the phenyl- $\alpha$ -naphthylamine was still present on the column. On streaking the column with the ammonium vanadate reagent, the phenyl- $\alpha$ -naphthylamine zone was clearly indicated by the development of the characteristic green color.

*Phenyl- $\beta$ -naphthylamine.*—As with phenyl- $\alpha$ -naphthylamine this material shows a vivid violet fluorescence in ultraviolet light which is clearly visible on an alumina column. The antioxidant is developed with pure benzene and is eluted quantitatively with this solvent. The red color developed with the nitric acid mixture, when used as a streak reagent, is sufficiently definite to enable the position of the zone to be identified on the column; the colors developed with the other reagents are inadequate for this purpose, but are of value as confirmatory tests on the isolated material. In view of the close similarity of the adsorption affinities of the  $\alpha$  and  $\beta$  compounds, it was expected that separation of a mixture of the two would be difficult and would require an abnormally long column. This was confirmed when a mixture of equal parts of  $\alpha$ - and  $\beta$ -naphthylamine was recovered unchanged after elution from a 6-inch alumina column. No separation into two zones could be observed when the column was viewed in ultraviolet light. This observation confirms the unsuitability of the mixed chromatographic method for the identification of substances which are only weakly adsorbed, unless special precautions are taken.

*Agerite White.*—This compound, stated to consist essentially of *sym-N,N*-dinaphthylphenylene diamine, shows a strong blue fluorescence in ultraviolet light. On adsorption on alumina and development with benzene, the movement of the zone can be clearly followed in this way and material of the accepted melting point is recovered quantitatively from the eluate. In addition, an extruded column containing adsorbed Agerite White was found to give a vivid blue color on streaking with the ammonium vanadate reagent.

However, this material has two other characteristics which simplify its identification. On exposure to light the original white material develops a strong purple tint due to colored decomposition products. On chromatographing this exposed material a variety of colored zones is obtained. The bulk of the Agerite White passes through as before in benzene, but is now visible on the column as a pink zone with a strong purple trailing edge. However, two further zones which are bright green and bright light blue remain firmly held at the top of the column and are not eluted with benzene. The detection of these zones on chromatographing the material after exposure to light should, therefore, afford a means of identification of Agerite White, and owing to the fact that some zones are now strongly absorbed, a mixed chromatogram also becomes possible. Although the amount of decomposition is, in fact, small, this observation indicates the desirability of shielding materials from light during the entire operation.



The second characteristic of this material is the intense red color developed on standing with cobalt oleate solution. On chromatography this red product passes out in benzene as a strong red zone followed by a grey zone, while the excess cobalt oleate remains at the top of the column. This observation emphasizes the necessity of separating the antioxidant completely from the accelerator before the latter is tested with cobalt oleate, as otherwise the masking effect due to the red color given by this antioxidant would completely mask that produced by the accelerator.

*Neozone-HF.*—This material in its common commercial form is a black-brown substance and appears to be a complex mixture. It shows a blue fluorescence in benzene and when adsorbed on an alumina column. This fluorescent band is readily eluted with benzene to give a pale brown material, which melts over a range of temperature and does not appear to be a single substance. This material represents the bulk of the antioxidant, although small brown zones are eluted with 1-alcohol-99-benzene, and with absolute alcohol. The quantity of material present in these zones is, however, so small that they can clearly be regarded as minor impurities.

That portion of the column which contains the fluorescent band gives a brilliant green color with the ammonium vanadate streak reagent, as does the material eluted with benzene. The color is sufficiently distinctive to enable this antioxidant to be differentiated from the others so far tested, especially in conjunction with the red brown given by the nitric acid reagent.

*Flectol-H.*—This material, which is reported to be an acetone-aniline condensation product, is supplied as a cream colored powder which fluoresces in ultraviolet light and which dissolves in benzene to give a pale yellow solution. On adsorption on alumina and development with benzene, a fluorescent fraction is eluted, but the quantity is a small fraction of the whole. The main bulk of the Flectol-H is eluted with 1-alcohol-99-benzene as a narrow brown zone, and a further small fraction is eluted with absolute alcohol as a pale blue zone.

This antioxidant, therefore, differs from the others previously examined, in that the bulk of it is retained on the column on development with benzene, but with 1-alcohol-99-benzene development is rapid, the zone moving at almost the same speed as the solvent front.

The brown zone which contains the bulk of the antioxidant gives, on removal of the solvent, a pale yellow solid which melts over a wide temperature range, indicating that it is probably a complex mixture. The colors given by the vanadate and dichromate reagents are too indeterminate to be of assistance in identification, but a strong red color is given by the nitric acid reagent.

*Agerite Stalite.*—This material is also a complex mixture and shows some fluorescence in benzene when exposed to ultraviolet light. The bulk of the antioxidant passes fairly rapidly through an alumina column on development with benzene, although secondary, and much smaller zones, are subsequently eluted with 1-alcohol-99-benzene, 5-alcohol-95-benzene and with absolute alcohol. The purified material after removal of the solvent is a pale brown-green liquid which gives a characteristic brown-ochre color with the dichromate reagent and a strong green with the nitric acid mixture.

*B.L.E.*—This material, also a mixture, shows a green fluorescence in benzene and is readily adsorbed on an alumina column as a black band at the top with a light brown zone below. On development with benzene a pale yellow zone is eluted; this, on removal of the solvent, contains the bulk of the material present. This fraction gave little fluorescence but gave strong positive color

reactions with the streak reagents described. The zone could also be detected on an extruded column by streaking with the same reagents.

On further development of the original column with 1-alcohol-99-benzene, a brown zone followed closely by a blue zone was developed, the brown zone splitting into two closely positioned zones further down the column. With absolute alcohol a dark blue band was developed, but in all cases the quantity of material was very small and these zones are clearly due to the presence of impurities.

#### DISCUSSION OF RESULTS

From the above results it will be seen that the antioxidants tested, with one exception, are only weakly adsorbed on alumina from benzene solution, and no difficulty should therefore arise in their separation from those components of a vulcanizate which are more strongly adsorbed. The exception, Flectol-H, is so rapidly eluted with 1-alcohol-99-benzene that it would be readily separable from more strongly adsorbed components, including accelerator residues. As will be shown later, such separations have, in fact, been realized on extracts from vulcanizates and the antioxidants have been cleanly separated from the accelerator components by use of this technique. In many cases the presence of impurities results in the detection of a number of other zones containing relatively small amounts of material, but these are, in general, unlikely to interfere seriously with the identification of other components, although their existence must be borne in mind in the examination of vulcanizates for the presence of decomposition products.

The separation of the antioxidants from paraffin wax and(or) mineral oil should not be unduly difficult since those tested appear to show some degree of adsorption, and in the cases of the materials examined the position of the zone can be determined by the use of streak reagents. On the other hand, to obtain a clean separation of these components it is necessary to use a somewhat longer column than is normally required.

For many laboratory purposes, the separation of the wax-antioxidant mixture free from other components of the vulcanizate is all that is necessary, since the color reactions described are not affected by the presence of the wax. Identification, therefore, becomes possible without further separation and all that is necessary is a simple chromatograph in which the whole of the benzene eluate is separated as a single fraction.

In any case, until such time as further means of identification are available, there is little to be gained in most cases by chromatographing the antioxidant free from wax, as, apart from the spot tests, there is no means of identification of the antioxidant fraction when it is eventually isolated.

#### IDENTIFICATION OF CERTAIN ANTIOXIDANTS IN VULCANIZATES

In previous sections of this work it has been shown that the method of chromatographic analysis can be used successfully in the identification of a number of common commercial accelerators in simple mixes and the behavior of single antioxidants on chromatographic columns, and methods of their identification have been described.

This work has now been further extended to a study of the detection of antioxidants in vulcanizates, and in this case different accelerators have also been included in the mix to demonstrate that the method permits of the identification of both components without mutual interference.

For this purpose, the mixes shown in Table I were prepared, vulcanized to the approximate optimum cure, and after suitable preparation extracted with acetone.

TABLE I

	A	A <sub>1</sub>	B	B <sub>1</sub>	C	C <sub>1</sub>	D	D <sub>1</sub>	E	E <sub>1</sub>	F	F <sub>1</sub>	G	G <sub>1</sub>	Blank	Blank
Pale crepe rubber	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Paraffin wax	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Stearic acid	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5
Sulfur	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
M.B.T.	0.25	—	0.25	—	0.25	—	0.25	—	0.25	—	0.25	—	0.25	—	0.25	—
D.P.G.	—	0.25	—	0.25	—	0.25	—	0.25	—	0.25	—	0.25	—	0.25	—	0.25
Agerite White	0.5	0.5	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Phenyl- $\alpha$ -naphthylamine	—	—	0.5	0.5	—	—	—	—	—	—	—	—	—	—	—	—
Phenyl- $\beta$ -naphthylamine	—	—	—	—	0.5	0.5	—	—	—	—	—	—	—	—	—	—
Flectol-H	—	—	—	—	—	—	0.5	0.5	—	—	—	—	—	—	—	—
Neozone-HF	—	—	—	—	—	—	—	—	0.5	0.5	—	—	—	—	—	—
Agerite Stalite	—	—	—	—	—	—	—	—	—	—	0.5	0.5	—	—	—	—
B.L.E.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

Two base mixes were employed and each of these was compounded with a number of the more common antioxidants. As in our earlier work the range of antioxidants has been restricted to a few common types, but these include both commercially pure chemicals and more complex mixtures.

In each case the acetone extract was evaporated to dryness, dissolved in benzene, and chromatographed on alumina. Except for Mixes D and D<sub>1</sub> (Flectol-H), the columns were then developed with benzene until both the wax and the antioxidant had been eluted: with the M.B.T. mixes this was a simple matter, since only these two components are developed with this solvent, but with those containing D.P.G. it was necessary to separate them from the red zone previously shown to be developed with benzene from the accelerator fraction. In practice, however, little difficulty was experienced, since the rate of development of the antioxidant was considerably greater than that of this zone, as shown by viewing in ultraviolet light and by the application of streak reagents.

The procedure with the Flectol-H mixes (D and D<sub>1</sub>) was rather different, since this antioxidant is not developed by benzene, and it will therefore be described in detail later.

In all cases, however, once the antioxidant and wax zones had been removed, the material remaining on the column was examined for the presence of accelerators by the methods previously described. In no case was any difficulty experienced in the satisfactory identification of either the M.B.T. or the D.P.G.; the former gave a strong green color with cobalt oleate, which showed the typical behavior on chromatography previously described; all the D.P.G. mixes showed the highly complex pattern of colored zones characteristic of this accelerator. In this connection it is interesting to note that none of the antioxidants gave any colored zones which might lead to confusion with D.P.G.

In one case (Agerite White) the authors have carried the chromatograph further and, with the aid of a second column, have shown that it can be cleanly separated from the wax. This was done to demonstrate the suitability of the technique for this purpose, but such separations are of little practical value with those antioxidants which are complex products, since even when separated from wax, their identification must still rest on the application of the same color reactions as can be applied to the wax mixtures. In this connection, however, the colors were, in some cases, rather slower in development when

wax mixtures were used, presumably due to the protective action of the wax, but on rubbing with a glass rod, satisfactory results were obtained.

#### IDENTIFICATION OF ANTIOXIDANTS IN VULCANIZATES

When the above mixes were examined chromatographically the following results were obtained.

*Blank mixes containing no antioxidant.*—The results obtained were, of course, strictly comparable with those already reported, and no difficulty was experienced in the identification of either the M.B.T. or the D.P.G. Only the wax portion was found to pass through with benzene in the case of the M.B.T. mix, whereas with the D.P.G. mix, this was followed much more slowly by the red zone derived from the accelerator. In all the subsequent mixes examined the accelerators were detected with equal facility without interference from the antioxidant.

*Mixes A and A<sub>1</sub>, containing Agerite White: Mix A.*—A relatively simple chromatogram was obtained with the extract from this vulcanizate, but it differed from those previously described and from the other M.B.T.-antioxidant mixes, in that some coloring matter was present, due to slight decomposition of the antioxidant, either during vulcanization or in the subsequent extraction. The colored materials present were those already described as being produced from Agerite White under the influence of light, and the zones produced are so specific and so different in chromatographic behavior from the complex pattern given by D.P.G. mixes that there is no danger of confusion arising. As previously shown, the pink and purple decomposition products are adsorbed to much the same extent as the antioxidant itself and serve, therefore, as a marker for the position of the latter on the column. The chromatograph therefore showed an initial yellow wax zone passing through rapidly with benzene, followed by a pink zone with a purple trailing edge which contained the antioxidant. A preliminary separation of these zones was therefore affected, and the pink-purple fraction was immediately rechromatographed on a second alumina column to free it completely from any contamination with wax. The necessity for this second operation depends, of course, on the length of the column originally used, and a clean separation can be obtained at once if a sufficiently long column is used initially.

On removal of the solvent from the purified fraction containing the antioxidant, pure Agerite White was obtained, and its identity confirmed by melting point determinations, both alone and on admixture with an authentic specimen. Further confirmation was obtained by the following tests. (1) It gave an intense red color on standing with cobalt oleate solution. (2) The behavior on chromatography of the cobalt oleate mixture obtained above was identical with that previously noted as being characteristic of the complex produced with Agerite White, and on the addition of an authentic specimen a mixed chromatograph gave an exactly similar result without any additional zones, or separation into two of any zone previously present. (3) On chromatography of the product after exposure to light, a pink zone with a purple trailing edge passed through in benzene, leaving two brightly colored zones (green and blue) firmly held at the top of the column. The material present in these latter zones is clearly produced by the action of light, as the original material had all been developed with benzene from a similar alumina column. This behavior is identical with that described for Agerite White and, in addition, a mixed chromatogram with authentic material which had been similarly exposed gave an identical result.

It is, therefore, clear that the method permits the isolation of the antioxidant, free from contamination with all other compounding ingredients.

*Mix A<sub>1</sub>.*—The complex chromatogram typical of D.P.G. vulcanizates was obtained, and while, as before, the antioxidant passed through on development with benzene and was readily separable from the wax, it was closely followed by the red zone originating from D.P.G. However, it could be separated from this, and the antioxidant so obtained gave the three color reactions for Agerite White.

To confirm the usefulness of the color reagents for streak tests, further columns were prepared with the above mixes, and were extruded before the antioxidant had passed out. The position of the antioxidant zone could then be readily determined by streaking with these reagents. The fluorescence shown by this material in ultraviolet light is also an excellent method of following the development of the antioxidant zone where other fluorescent materials are known to be absent.

*Mixes B and B<sub>1</sub> containing phenyl- $\alpha$ -naphthylamine.*—In both cases the chromatographs obtained were essentially similar to the comparable ones given by Agerite White, with the exception that no colored decomposition products of the antioxidant were noted. In each case the development of the chromatogram could be followed by inspection in ultraviolet light or by the use of streak reagents, and no difficulty was experienced in separating the antioxidant-wax mixture from all other components. On application to this fraction of the three color reactions described strong green colors of similar intensity to those developed with authentic phenyl- $\alpha$ -naphthylamine were obtained.

*Mixes C and C<sub>1</sub> containing phenyl- $\beta$ -naphthylamine.*—The results obtained were closely similar to those given with the  $\alpha$  derivative. Again, the development of the antioxidant zone could be readily followed by ultraviolet light or, in this case, by the use of the nitric acid reagent. The wax-antioxidant mixture was obtained free from other components, and in both cases gave satisfactory color tests for the presence of phenyl- $\beta$ -naphthylamine with the three color reagents described.

*Mixes D and D<sub>1</sub> containing Flectol-H.*—The treatment of the initial chromatogram to isolate the antioxidant was rather different with these mixes, since Flectol-H has been shown previously to resist development with benzene. Accordingly, the initial chromatograms from both mixes were thoroughly washed with benzene, thereby removing the wax, and the separations were continued as follows.

*Mix D.*—After removal of the wax, development of antioxidant was then commenced with 1-alcohol-99-benzene. M.B.T. is developed only slowly with this solvent, whereas Flectol-H is developed rapidly. No difficulty was, therefore, experienced in separating this material in a clean state, leaving the accelerator on the column. The antioxidant zone was clearly visible as a pale yellow-brown zone moving rapidly down the column, and on examination of this fraction satisfactory color reactions for Flectol-H were obtained.

*Mix D<sub>1</sub>.*—In this case it was necessary to continue the benzene washing until the red zone due to D.P.G. had also been removed from the column. The antioxidant was then developed with 1-alcohol-99-benzene, when it was found that it could be readily separated from other more slowly moving components. Identification of the fraction obtained was satisfactorily achieved with the spot tests.

The removal of the red zone due to D.P.G. is laborious and could probably be omitted, for the authors have previously shown that the amount of material



present in this zone is small. Furthermore, preliminary tests indicate that it is unlikely to interfere with the color reactions described.

*Mixes E and E<sub>1</sub> containing Neozone-HF.*—The chromatograms from the extracts from the vulcanizates were again quite simple, and similar to those given by the phenyl-naphthylamines. The development of the antioxidant zone with benzene could be readily followed in each case by the use of streak tests, and satisfactory identification of the Neozone-HF was subsequently made by the application of the color tests to each of the antioxidant-wax fractions. In the case of Mix E<sub>1</sub> the antioxidant zone was well clear of the slower moving red zone which was also developed by benzene, and no difficulty was experienced in separation.

*Mixes F and F<sub>1</sub> containing Stalite.*—The chromatograms obtained from both extracts were again quite straightforward, and the progress of the Stalite down the column could be followed by streak reagents. It was readily separated from all other components except the paraffin wax, and the mixtures with wax so obtained gave satisfactory positive color reactions in each case, thus enabling the Stalite to be identified.

*Mixes G and G<sub>1</sub> containing B.L.E.*—Again the chromatograms from both extracts were quite straightforward, and the B.L.E.-wax fractions were separated from other components without difficulty. The passage of the antioxidant could again be followed successfully with streak reagents, and satisfactory results were obtained in the identification of the B.L.E. present in the extracts by the color reactions described.

#### DISCUSSION OF RESULTS

It is clear that the antioxidants studied can be readily separated from the other components of the mix, with the exception of the wax and(or) mineral oil component, but, as has been shown, there is no inherent difficulty even in this, although it may involve the use of a long column, and is probably unnecessary for most purposes. By the use of this technique it is practicable to separate and identify certain accelerators and antioxidants from a vulcanizate.

#### SUMMARY

The work is still in a preliminary stage, but sufficient has now been done to demonstrate the applicability of chromatographic methods to rubber analysis. The acetone extracts of vulcanizates are complex mixtures not readily amenable to analysis by normal chemical methods. By the use of this elegant technique, however, it has been possible to effect the efficient separation of wax, fat acids, accelerators, and antioxidants, not only from each other but also from naturally occurring coloring matter and from degradation products. The subsequent identification of the main fractions is then a relatively simple matter, as tests such as the cobalt oleate reaction for accelerators and the spot reactions for antioxidants can be applied without interference from any other components.

The elegance of the method is further demonstrated by the fact that it can be used in the identification of components present in much smaller quantities than are detectable by other chemical methods.

The accelerators and antioxidants studied so far are rather limited in number, but cover the main classes of these materials, and the method should, therefore, be applicable to the analysis of a number of technical vulcanizates, and the authors have, in fact, already made use of it with some success for this purpose.



It is noteworthy that the adsorption and elution processes are quantitative, and that the whole of the material put on to a column can, therefore, be recovered from the various fractions. This, therefore, offers the possibility of quantitative work on such problems as the rate of consumption of accelerators during cure or the relationship of antioxidant content to behavior on aging. Such work would necessarily be restricted to experiments using pure accelerators and pure antioxidants which are single chemical entities.

In this connection the degradation products obtained from mixes accelerated with T.M.T. or M.B.T.S. or D.P.G. are of interest both in the actual isolation of the components in question and in partial confirmation of the work of others in this field.

A much more intensive study of the degradation products of each accelerator in mixes cured to varying degrees may well throw more light on the complex subject of accelerators.

Although, therefore, the authors have been able to show the utility of chromatography for their own particular analytical problems, it is likely, ultimately, to be of great value in the exploration of some of the fundamental problems of rubber chemistry.

#### ACKNOWLEDGMENT

The authors' thanks are due to the Chief Scientist, Ministry of Supply, for permission to publish this paper.

#### REFERENCES

- <sup>1</sup> Caspari, "India Rubber Laboratory Practice", Macmillan, London, 1914; Luff, "The Chemistry of Rubber", Ernest Benn, Ltd., London, 1923; Weber, "The Chemistry of Rubber Manufacture", Charles Griffin & Co., London, 1926; "The Science of Rubber", edited by Memmler, translated by Dunbrook and Morris, Reinhold Publishing Corp., New York, 1934; "The Chemistry and Technology of Rubber", edited by Davis and Blake, Reinhold Publishing Corp., New York, 1937; Am. Soc. Testing Materials, Standards on Rubber Products.
- <sup>2</sup> British Standard Methods of Testing Vulcanized Rubber, B.S. 903 (1940).
- <sup>3</sup> Services Rubber Investigations. Users Memorandum U.9.
- <sup>4</sup> Callan and Stafford, *J. Soc. Chem. Ind.* **1924**, p. 43.
- <sup>5</sup> Shimada, *J. Soc. Chem. Ind. Japan* **36**, 82 (1933); *J. Soc. Rubber Ind. Japan* **5**, 420 (1932).
- <sup>6</sup> Wistinghausen, *Kautschuk* **5**, 57, 75 (1929).
- <sup>7</sup> Cajelli, *Gomma* **3**, 1 (1939).
- <sup>8</sup> Levi and Giera, *Gazz. chim. ital.* **67**, 719 (1937); Levi and Cajelli, *Rev. Brasil chim.* (Sao Paulo) **8**, 119, 161 (1939).
- <sup>9</sup> Levi and Giera, *Gazz. chim. ital.* **67**, 719 (1937).
- <sup>10</sup> Zechmeister and Cholnoky, "Principles and Practice of Chromatography", translated by Bacharach and Robinson, 1943.
- <sup>11</sup> Strain, "Chromatographic Adsorption Analysis", 1945.
- <sup>12</sup> Kreps, *J. Rubber Ind.* (U.S.S.R.) **9**, 45 (1935).
- <sup>13</sup> Callan and Stafford, *J. Sci. Instruments* **1924**, p. 43.
- <sup>14</sup> Turk and Reed, *Ind. Eng. Chem. Anal. Ed.* **17**, 713 (1945).
- <sup>15</sup> Dufraisse and Jarrijon, *Compt. rend.* **215**, 181 (1942).

## DEVICE FOR EVALUATING SURFACE CRACKING OF GR-S \*

M. C. THRODAHL

MONSANTO CHEMICAL COMPANY, NITRO, WEST VIRGINIA

The scope of this paper is limited to a study of the surface cracking on a GR-S vulcanizate dynamically stretched at periodic intervals. Abundant literature<sup>1</sup> on experimental techniques and interpretation of the mechanism of surface cracking indicates marked variance of opinion, but most authors agree that the presence of ozone is necessary to surface cracking. However, Williams<sup>2</sup> showed that ultraviolet light activated formation of a skin on the surface of stretched rubber and that this protected the interior from continued crack growth. In the evaluation of materials designed to minimize or retard the rate of crack growth, the static A.S.T.M. test<sup>3</sup> indicated that those showing blooming tendencies apparently provided a surface film, which in turn inhibited deterioration beneath the surface. Although it has apparently been established that ultraviolet light itself does not cause surface cracking<sup>4</sup>, GR-S vulcanizates exposed to periodic surface changes under strain crack badly in the presence of it. Although this mechanism is not thoroughly understood, it was thought worthy of further investigation, especially in view of the fact that most studies on surface cracking were made on statically exposed specimens.

### FLEXING DEVICE

The flexing mechanism shown in Figures 1, 2, and 3 is designed on the assumption that a dynamically stretched surface increases the probability of crack formation and increases the rate of growth of those already formed. A double turntable fixed to a double cam provides angular motion, which ensures uniformity of radiation; it also causes linear displacement, which is necessary to stretch the surface of the specimens. Ordinary dumbbell tensile specimens<sup>5</sup> are stretched over specially designed pins and stirrups (Figure 3) arranged concentrically (Figure 2) near the outer diameter of a turntable consisting of two 17-inch diameter circular plates. The top turntable rotates in a fixed plane.

A study of the variables of the flexing device involved the following factors: angular velocity of turntable, linear displacement or percentage strain of specimen, intensity of radiation, and time of exposure.

Angular velocity was arbitrarily selected at 24 revolutions per minute because its function was only to provide constant rate of change of position to allow each specimen a constant exposure. Reduction in angular velocity was obtained with a vertical-drive Boston gear reducer with a 43 to 1 capacity. Linear displacement was varied by means of removable pins holding small stirrups over which the specimens flexed. The length of these pins determined the amount of strain or linear displacement, which was finally established at

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 39, No. 4, pages 514-516, April 1947. This paper was presented before the Division of Rubber Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, N. J., April 10-12, 1946.

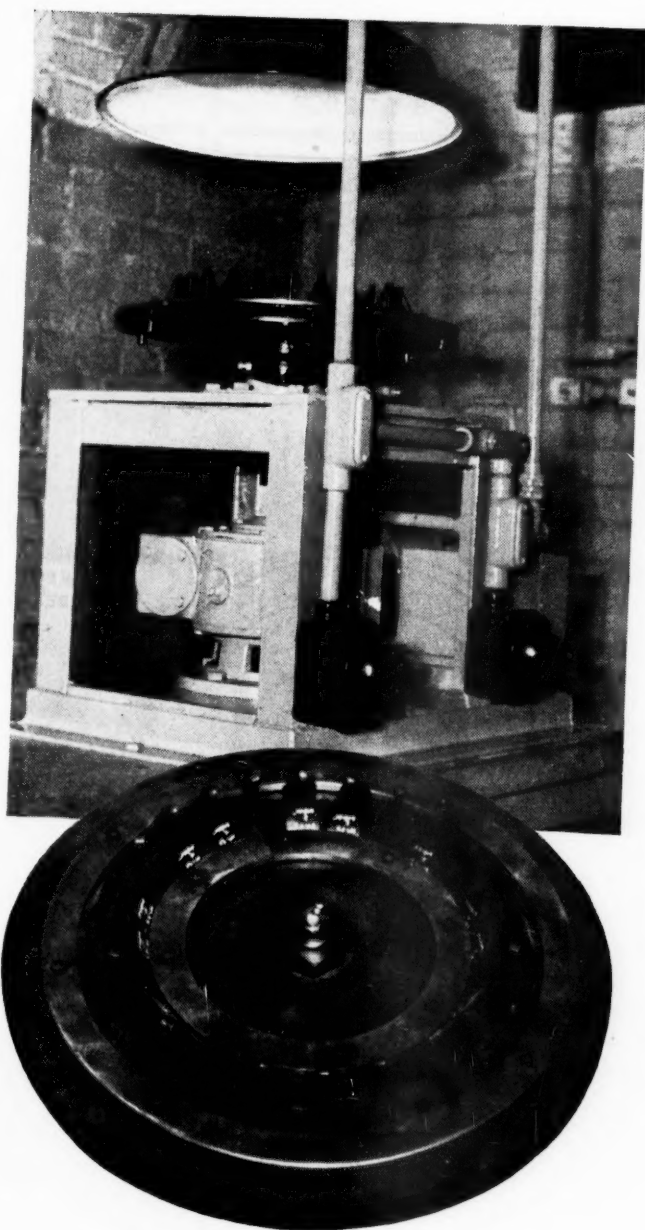


FIG. 1.—Dynamic flexing apparatus, with turntable  
(below) showing specimens in place.

ing on a  
abundant  
mechanism  
authors  
however,  
on the  
continued  
or retard  
showing  
turn in-  
tly been  
GR-S  
ly in the  
l, it was  
act that  
mens.

on the  
bility of  
formed.  
which en-  
which is  
l tensile  
figure 3)  
ble com-  
ates in a

factors:  
train of

nute be-  
sition to  
city was  
capacity.  
g small  
etermined  
ished at

April 1947.  
American

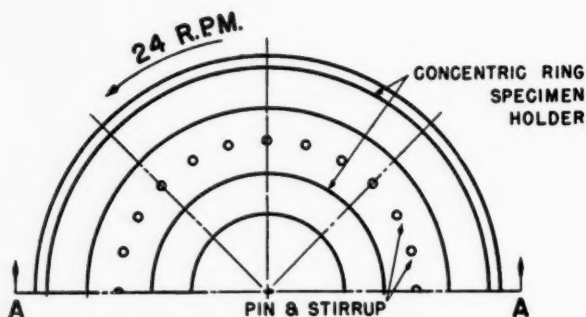
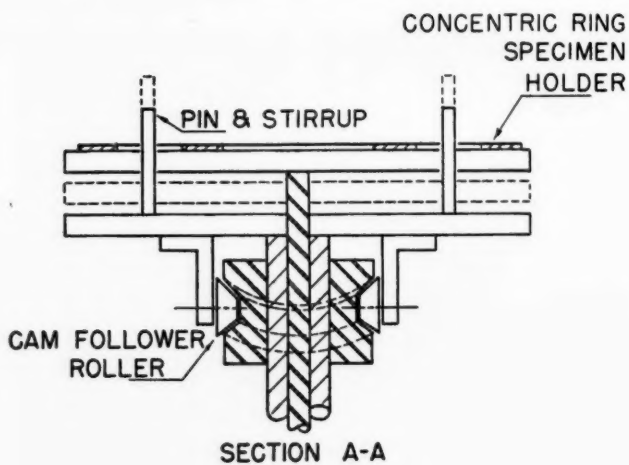


FIG. 2.—Schematic diagrams of flexing mechanism.

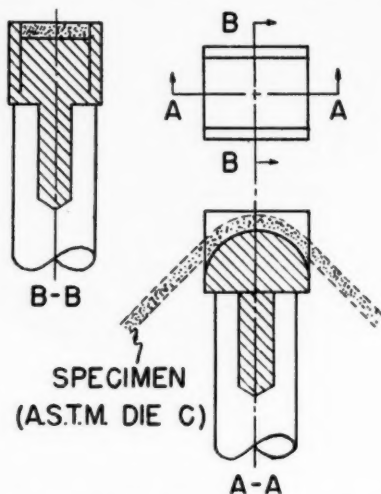


FIG. 3.—Schematic diagram of pin and stirrup.

$\frac{5}{16}$  inch, causing a 35 per cent strain in the specimens. Ultraviolet light was generated by a type S-1 sun lamp manufactured by the General Electric Company. Data are reported<sup>6</sup> which show the wave length distribution of the S-1 lamp to be nearly equivalent to that of natural sunlight. The reflector was mounted on a boom held vertically over a distance of 100 cm. from the turntable top. Exposure time for a selected fixed height of the light source varied, but definite cracking was observed after 50 hours of dynamic exposure. Most data, however, were taken at 100 hours of exposure; this period was sufficient to cause surface cracking on the best of stocks.

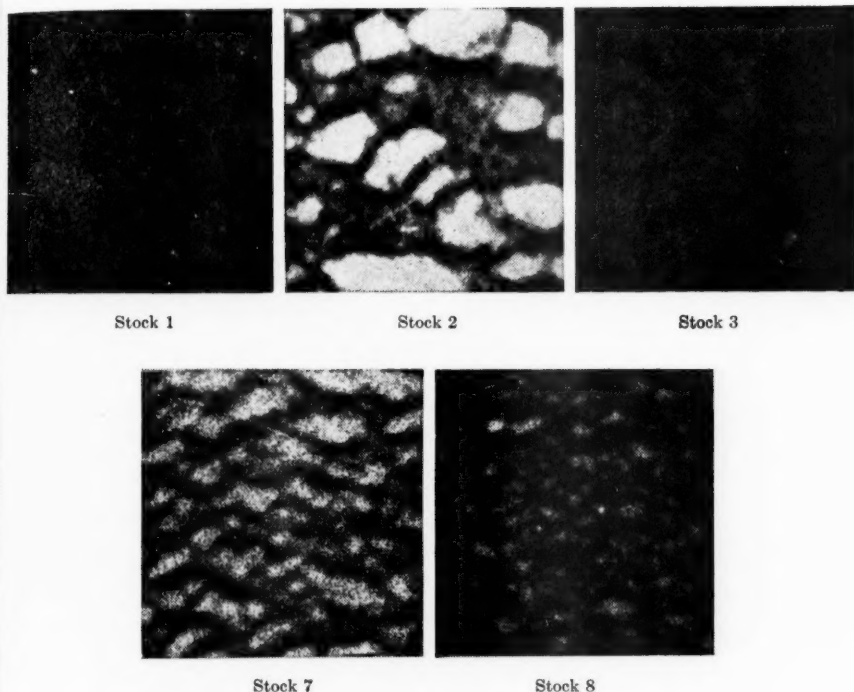


FIG. 4.—Effect of 100-hour dynamic exposure to S-1 lamp on GR-S tread stocks stretched to 100% elongation and surface-dusted with talc for photographs ( $\times 7$ ).

Figure 4 shows the effect of the method on the cracking characteristics of GR-S tread stocks containing typical additives for reducing the rate of surface cracking. Typical stock compositions and observations on surface cracking are shown in Tables I and II.

### CONCLUSIONS

1. Dynamic flex-cracking may be studied indoors under conditions which yield results closely comparable to outdoor atmospheric exposure.
2. Although the photographs are not sufficient to show the depth of cracking, it was observed that the stocks of several compounds which showed the tendency to bloom and migrate to the surface cracked badly and to a depth equivalent to control stocks. By comparison, however, these same stocks

TABLE I  
COMPOSITION OF GR-S STOCKS CURED 90 MINUTES AT 142° C

Base formula		Parts
GR-S		100.0
Channel black (Kosmobile-77)		40.0
Zinc oxide		3.0
Softener (Paraflex)		8.0
Sulfur		1.75
<i>N</i> -Cyclohexyl-2-benzothiazole sulfenamide		1.2

Additive	Stock number				
	1	2	3	7	8
Benzidine-acetone condensation	1.0	..	..	..	..
4- <i>tert</i> -Butyl- <i>m</i> -cresol monosulfide	..	1.0	..	..	..
<i>p</i> -Phenetidine-acetone condensation	..	..	1.0	..	..
Protective wax	..	..	..	1.0	..

TABLE II  
OBSERVATION OF DYNAMIC SURFACE CRACKING OF GR-S TREAD STOCKS

Stock	Condition of surface cracking after dynamic exposure to S-1 lamp		Condition of surface cracking after dynamic exposure in July atmosphere
	50 hours	100 hours	
1	None	Very slight on top surface, very slight bottom surface	Slight on both surfaces
2	Deep, wide on top surface above stirrup; slight on bottom surface	Severe cracking on both surfaces	Severe on both surfaces
3	None	Very slight on top surface; none on bottom surface	Slight on top surface; Very slight on bottom surface
7	Slight top surface, slight bottom surface	Deep, fine cracking on both surfaces	Deep on both surfaces
8	Deep, wide on top surface above stirrup; slight on bottom surface	Deep, coarse on top surface; coarse on bottom surface	Deep, coarse on both surfaces; very severe

when statistically exposed showed only slight tendency to crack in the usual exposure time of 100 hours.

3. Minimum concentration of additives for retarding the rate of surface cracking was found to be 0.25 per cent, but best results were obtained with 1 per cent.

4. Cracking always occurred at right angles to the direction of strain.

Preliminary studies with this apparatus indicated that none of the specimens cracked when exposed in the looped but unstretched position (this was done by removal of the pin and stirrup) up to 50 hours of exposure, but some cracked slightly at 100 hours. Flexing in the laboratory without the source of ultraviolet light did not produce cracking of the specimen in 100 hours. The nature and severity of cracking were made the same for natural sunlight outdoor exposure in July as they were for artificially generated conditions of the laboratory except that approximately 3 weeks (roughly 60 exposure hours) were required. (This overall time was due to excessive rain, which necessitated coverage of the entire flexing mechanism during much of the time.) This may



not be a fair comparison because of the rather contaminated atmospheric conditions in Nitro, W. Va. However, stocks of the same composition flexed on a revolving belt in Florida atmosphere cracked in the same manner as those shown here<sup>7</sup>.

Variation of degree of strain from 10 to 35 per cent did not produce significant differences in results. This is in agreement with the observations of Powell and Gough<sup>8</sup>, who pointed out that the so-called critical stretch does not exist.

Change in height of the light source—that is, the radiation intensity—over the short range did not produce significant changes in rate of cracking. In order that the surface temperature of the stock remains at 30–35° C, the minimum height was fixed at 50 cm. above the turntable.

#### REFERENCES

- <sup>1</sup> Am. Soc. Testing Materials, Standards, D518-44 (1944); Newton, *J. Rubber Research* **14**, 27, 41, 62 (1945); RUBBER CHEM. TECH. **18**, 504 (1945); Powell and Gough, *Trans. Inst. Rubber Ind.* **21**, 102 (1945); RUBBER CHEM. TECH. **19**, 406 (1946); Crabtree, James, and Kemp, *Ind. Eng. Chem.* **38**, 278 (1946).
- <sup>2</sup> Williams, *Ind. Eng. Chem.* **18**, 367 (1926).
- <sup>3</sup> Am. Soc. Testing Materials, Standards D518-44 (1944).
- <sup>4</sup> Newton, *J. Rubber Research* **14**, 27, 41, 62 (1945); RUBBER CHEM. TECH. **18**, 504 (1945).
- <sup>5</sup> Am. Soc. Testing Materials, Standards D412-41 (1941). Die C.
- <sup>6</sup> Luckiesh, "Artificial Sunlight", Van Nostrand Co., New York, 1930, p. 69, Table VI, p. 248, Plate 1; Weitz and Amick, General Electric Co., Nela Park Eng. Div., Folder H (Apr. 1945).
- <sup>7</sup> Baker, D. E., Monsanto Chem. Co., private communication.
- <sup>8</sup> Powell and Gough, *Trans. Inst. Rubber Ind.* **21**, 102 (1945); RUBBER CHEM. TECH. **19**, 406 (1946).

## CRUDE RUBBER PREPARATION

### SHEET PRODUCTION BY CONTINUOUS COAGULATION OF HEVEA LATEX \*

E. B. NEWTON, W. D. STEWART, AND E. A. WILLSON

MALAYAN RESEARCH LABORATORIES, THE B. F. GOODRICH COMPANY, KUALA LUMPUR  
FEDERATED MALAY STATES

The widespread use of dilute acid as the principal coagulant for Hevea latex in the rubber plantation industry is due to a suggestion of Biffen<sup>1</sup>, who, during an investigation of the type of smoke used in the Brazilian method of rubber preparation, found acetic acid to be the chief component of the aqueous condensate.

The reaction of fresh Hevea latex to the addition of dilute acids is quite different from that of ammonia-preserved latex as received in this country. (In this discussion the term "fresh latex" denotes latex not more than 12 hours old, counting from the time of tapping the tree.) When ammonia-preserved latex is acidified, coagulation is essentially instantaneous at the spot on the latex surface where the dilute acid falls. But in the case of fresh latex, flocculation occurs, and the mix, although thickened, can still be stirred with gentle action to distribute the coagulant adequately throughout the entire batch. More than an hour later these flocs begin to fuse into a solid coagulum, but it is not until some hours' standing, usually overnight in Malayan practice, that this coagulum is strong enough to withstand without undue deformation the handling attendant on machining it into wet sheet—the process of putting the slabs of coagulated latex through a series of close-set rolls (sheeting battery) to squeeze out rubber-free serum.

Where the daily output of rubber amounts to only a few pounds, as is the case with many small holders (operators of less than 100 acres of rubber trees), coagulation is carried out in individual pans of about 1 Imperial gallon capacity, yielding 1.5 pounds of rubber sheet (dry basis). Where large volumes of latex are to be converted, as in estate practice, coagulation is run in rectangular tanks of 200 to 220 Imperial gallons capacity, a standard size being 10 feet long, 3 feet wide, and 15 inches deep. Inside these tanks along their length, vertical slots are cut every 1.5 inches so that, after the acid coagulant is mixed with the diluted latex, solid separating sheets or partitions may be inserted. The acidified latex which subsequently coagulates is thus effectively shaped in slabs convenient for handling. Upwards of eighty of these partitions per standard tank must be inserted, removed, and kept clean every time a coagulation is run. On some very large estates the method of fitting the partitions in the coagulation tanks is modified so that only the opposite ends of alternate partitions touch the sides of the tank. With this system the coagulum forms in serpentine fashion in each tank. On removal of the partitions the coagulum can be withdrawn as a continuous ribbon and fed into a suitable sheeting battery. The

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 39, No. 8, pages 978-984, August 1947. The present address of E. B. Newton and E. A. Willson is The B. F. Goodrich Co., Akron, Ohio; that of W. D. Stewart is The B. F. Goodrich Co., Boyce-Thompson Institute, Yonkers, N. Y.

process is continuous only so far as the machining of coagulum from an individual tank is concerned. The rate of coagulum formation is not accelerated over that of the usual practice.

After a visit to Malaya in 1939, Stevens<sup>2</sup> commented that the method of sheet rubber production had not changed basically since the days of the pioneers, and suggested that a process of continuous coagulation and sheet formation should be available where large volumes of latex are converted into sheet rubber. In recent years patents have been issued describing rubber production by continuous coagulation methods applicable to fresh Hevea latex<sup>3</sup> and to synthetic latices<sup>4</sup>, including the salt-acid coagulation method<sup>5</sup>.

### COAGULATION OF HEVEA LATEX

The importance of coagulation phenomena from theoretical as well as practical viewpoints is evident on even casual examination of literature published since the turn of the present century.

Pertinent to the present discussion is an interesting chain of studies started by Whitby's observation<sup>6</sup> that fresh latex which has been sterilized by heating does not form a solid coagulum or clot on acidification with the usual proportion of acetic acid (to approximately pH 4.6 to 4.8). The latex particles merely flocculate and cream upward, but do not coalesce<sup>7</sup> into a clot even after 1 or 2 days' standing. (The term "coalescence" is used in this discussion in the same way de Vries employed it—namely, "the transition of a loose mass of flocs into a fixed gel".) Eaton and Grantham<sup>8</sup> observed that some latex which they had heat-sterilized in an autoclave did form a clot on acidification, but Barrowcliff<sup>9</sup> pointed out that as a result of their heating method, it is probable the temperature of the latex itself never reached that of the surrounding steam. The latter investigator, without the use of pressure equipment, prepared a modified latex similar to Whitby's by slowly pouring fresh latex into an equal volume of water at 90° C, with subsequent cooling to room temperature. Latex so treated (Barrowcliff latex) lost its ability to coalesce on acidification. He also observed, however, that the addition of a few drops of fresh latex to a small volume of Barrowcliff latex restored this ability. Whitby<sup>6</sup> had suggested that the heating destroyed a specific enzyme essential to coagulation, and Barrowcliff's inoculation technique lent support to this view. Campbell's experiments<sup>10</sup> led to a similar conclusion. Eaton and Grantham<sup>8</sup>, on the other hand, attributed the natural spontaneous coagulation of latex to bacterial action rather than to a specific enzyme, and it is noteworthy that acidified Barrowcliff latex forms a clot under tropical conditions after standing exposed to the air for upwards of a week.

De Vries and Beumée-Nieuwland<sup>11</sup> modified Barrowcliff's method to give a more dilute latex, B liquid, and found it possible to obtain from it a natural coalescence agent in this way<sup>12</sup>. B liquid<sup>13</sup> was inoculated with a few drops of fresh latex and then acidified to form a clot. The resulting coagulum, when dry, was soaked in dilute aqueous sodium carbonate. The extract so obtained could be used, interchangeably with fresh latex, as a coalescence agent for B liquid. It is of interest to note that, with a given coagulum, successful extraction of coalescence agent could not be repeated indefinitely. Conceivably, the sodium carbonate reacted with a portion of any free fat acids present in the coagulum to form sodium soaps, and these were the active agents.

Van Harpen<sup>14</sup> has provided an exhaustive review up to 1930 of natural and synthetic agents capable of causing coalescence or clot formation in acidified B

liquid. The treatise includes a series of reagents first used by that author, notably the ammonium soaps of oleic, palmitic, and stearic acids, and the ammonia-soluble portion as well as the alcohol-soluble portion of the acetone extract of crepe rubber, the latter being particularly active. Until the work discussed below was undertaken, no investigator appears to have applied coalescence accelerators together with adequate control of pH to the coagulation of fresh Hevea latex, either from the standpoint of theoretical interest or as a practical attempt to devise processes for continuous sheet production.

#### COALESCENCE ACCELERATORS IN FRESH LATEX

The problem of accelerating the rate of coagulation of fresh latex was first attacked empirically (Table I). The various acids to be tested for coalescence activity were dissolved in ammonia and added to the latex diluted to a dry rubber content (D.R.C.) of 2 per cent; this was then acidified with 2 per cent acetic acid. The general procedure of coagulation used in this study was carried out as follows:

*Method of coagulation.*—300 cc. of fresh latex were added to 300 cc. of tap water containing the coalescence agent, and this was then poured into 4000 cc. of tap water containing 80 cc. of 2 per cent acetic acid with stirring.

The time to coalesce was taken as the interval between addition of the latex and the time at which the flocculates actually began to form a continuous clot when the surface was moved with a spatula. The time to firm up was read when the coagulum no longer adhered to wetted fingers when slipped beneath the coagulum. The pH was determined by glass electrode, and coagulation was carried out at 2 per cent dry rubber content.

TABLE I  
VARIOUS ACIDS AS COALESCENCE ACCELERATORS

Material	Quantity* per 100 grams rubber	Time of coalescence† (min.:sec.)	pH of serum
Adipic acid	1.5	>3:00	4.33
<i>o</i> -Aminophenol sulfonic acid	1.9	>3:00	4.50
Azelaic acid	1.9	>3:00	4.68
<i>n</i> -Butyric acid	0.9	>3:00	4.71
<i>n</i> -Capric acid	1.7	0:10	4.70
Chloroacetic acid	0.9	>3:00	4.50
Gallic acid	1.7	>3:00	4.36
Glycine	0.8	>3:00	4.60
Glycolic acid	0.8	>3:00	4.25
Lactic acid	0.9	>3:00	4.60
Lauric acid	2.0	0:40	4.78
<i>dl</i> -Maleic acid	1.3	>3:00	4.11
Naphthenic acid	1.3	3:00	4.75
Oleic acid	2.8	0:20	4.77
Phenylacetic acid	1.4	>3:00	4.58
Phthalic acid	1.7	>3:00	4.50
Pyruvic acid	0.9	>3:00	4.69
Ricinoleic acid	3.0	0:01	4.87
Succinic acid	1.2	>3:00	4.40
Control			
Coconut fat acids (1% on rubber)	..	1:20	4.75
Fresh latex	None	About 45:00	4.70

\* Coalescence agents added to latex, on the basis of 0.01 molar equivalent per 100 grams of rubber, dissolved in 20% aqueous ammonia (about 0.75 ml.) per 100 grams rubber.

† Coalescence times of 3 minutes or less were regarded as preferable.

When the latex flocs began to stick together to form a continuous clot, the time was taken. This end point was considerably more definite than might be predicted by one who has not observed it. Readings could be reproduced within  $\pm 10$  per cent of the elapsed time, and even less on many occasions. With the preferred coalescence agents, a variation of  $\pm 10$  per cent in the time actually amounts to only  $\pm 3$  to 6 seconds.

The data in Table I show that, of the materials tried, the soapforming fat acids possess greatest activity. While the untreated latex requires about  $\frac{1}{2}$  hour for clot formation, addition of approximately 2 per cent of the active fat acids as soaps may reduce this time to only a few seconds.

#### COALESCENCE AGENTS OF HIGH ACTIVITY

Some of the reagents showing very fast acceleration are set forth in Table II. The pH of the serum must be adequately controlled just as it should be in good

TABLE II  
COALESCENCE AGENTS SHOWING FAST ACCELERATION

Coalescence accelerator	Percentage by weight on rubber	Time required to		pH of serum
		Coalesce (min.:sec.)	Firm up (min.:sec.)	
None (control)		30:00	60:00	4.62
$\beta$ -Naphthol*	0.5	0:45	2:45	4.90
	1.0	0:45	2:00	5.0
Lauric acid*	0.5	2:45	4:15	4.65
	1.0	0:55	2:15	4.81
	1.5	0:40	2:00	4.83
Stearic acid*	0.5	9:15	15:00	4.70
	1.0	7:30	12:00	4.79
	1.5	2:15	5:00	4.81
Lux soap flakes	None (control)	25:00	38:00	4.67
	0.10	17:30	22:00	4.72
	0.25	5:45	8:30	4.85
	0.50	2:45	3:00	4.84
	1.00	1:00	2:15	4.85
	1.50	0:40	2:15	4.94
Ricinoleic acid†	0.25	1:00	..	..
	0.50	0:20	..	..
	1.00	0:02	..	..
	2.00	0:01	..	..
	3.00	0:01	..	..

\* Added to latex as ammonium salts.

† Added to latex as sodium soap.

estate practice where clean-cut coagulation with clear (not milky) serum is the rule. This means the pH of coagulation should be less than 5, preferably in the range of pH 4.6 to 4.9. A small increase in acid is required to neutralize the alkalinity contributed by the coalescence agent as added. Particular reference is directed to the remarkable activity of ricinoleic acid. This material used in the range of 1 to 3 per cent on the rubber causes instantaneous local coagulation where the acetic acid solution (as coagulant) strikes the latex. Such coagulations gave milky serums because the coagulant could not be uniformly stirred in; but the coagulations using 0.5 and 0.25 per cent of this agent on the rubber were satisfactory in this respect.

## LOCALLY MADE SOAPS AS ACCELERATORS

Malaya is a large producer of both coconut oil and palm oil, the cheapest sources of fat acids available in that locality. Their utility was investigated. The mixed fat acids of each of these oils were isolated and, as sodium soaps, were tried as coalescence accelerators. In another case the entire saponification mixture was employed for the same purpose. The coagulant in these tests was 2 per cent acetic acid. Results recorded in Table III show that such

TABLE III  
COMPARISON OF CRUDE LAURIC AND PALMITIC ACIDS,  
WHOLE COCONUT OIL, AND WHOLE PALM OIL AS SOAPS

Coalescence accelerator	Percent- age by weight on rubber	$\frac{1}{2}$ N H <sub>2</sub> SO <sub>4</sub> * (cc.)	D.R.C. at coagu- lation	Time to		pH of serum
				Coalesce (min.:sec.)	Firm up (min.:sec.)	
Coconut oil fat acids	1	None	2	0:53	1:47	4.83
Palm oil fat acids	1	None	2	1:15	2:10	4.80
Whole coconut oil soap	1	None	2	0:50	..	4.90
Whole palm oil soap†	1	6	2	1:05	2:10	4.79
Whole palm oil soap†	1	7	2	0:47	1:35	4.78

\* To neutralize excess NaOH in the whole soap.

† Red bleached Malayan palm oil, 80 grams heated to 100° C; NaOH (includes 50% excess), 18 grams heated to 100° C; water, 36 grams heated to 100° C.

locally made soaps are entirely satisfactory in reducing time of coalescence to about 1 minute when they are used at a concentration of 1 per cent (fat acid basis) on the rubber. The procedure is as follows. Stir hot caustic solution into hot oil to effect a good emulsion. Heat gradually to 120° C (this takes 30 to 60 minutes) and use as 1 per cent solution. Gelling during dilution is avoided by keeping the soap solution at 60° to 70° C. Yield of fat acids (if isolated) is 75 to 75.5 grams from 80 grams of palm oil. Coconut oil soap was prepared in the same way.

Rubber produced with palm oil soap had less odor than that made with coconut oil soap.

## EFFECT OF VARIABLES ON RATE OF COALESCENCE

*Concentration of coalescence agent.*—These variations are shown in Table IV for whole coconut oil sodium soap alone as well as for mixtures of this with

TABLE IV  
EFFECT OF VARYING SOAP CONCENTRATION ON RATE OF COALESCENCE\*

Kind of soap	Percentage added on rubber	Time of coalescence (min.:sec.)	pH of serum
None	..	23:00	4.84
Coconut oil	0.25	7:20	4.70
Coconut oil	0.50	2:30	4.80
Coconut oil	0.75	1:30	4.82
Coconut oil	1.00	0:50	4.90
Coconut oil	2.00	0:20	..
Coconut oil	0.50	0:45	..
Ricinoleic acid	0.05		
Coconut oil	0.50	0:30	..
Ricinoleic acid	0.10		
Coconut oil	1.00	0:15	..
Ricinoleic acid	0.05		
Coconut oil	1.00	0:11	..
Ricinoleic acid	0.10		

\* D.R.C., 2% at coagulation; coagulant, acetic acid; coalescence agents, sodium soaps.



sodium ricinoleate. As little as 0.25 per cent of the former reduces the time of coalescence to one-third that of the untreated latex which, in this series, is already more sensitive than ordinarily encountered (probably because of a higher-than-usual bacteria count). Increased amounts of coalescence agent in the latex progressively decrease the time of coalescence. Hence, the rate of coagulation can be varied over a wide range (1) by choice of coalescence agent of suitable activity and (2) by the amount of this agent used in the latex. The inclusion of 1 per cent or so of fat acid during the preparation of rubber for general purpose compounding is regarded as beneficial rather than detrimental.

*Inorganic ions.*—Addition of barium, calcium, lead, magnesium, and zinc as acetates (1 per cent each on the rubber) to the coagulant accelerated the rate of coalescence of fresh untreated latex, coagulation being run at 2 per cent D.R.C. As shown in Table V, calcium, magnesium, and barium were active,

TABLE V  
EFFECT OF SEVERAL IONS ON RATE OF COALESCENCE\*

Ion†	Without coalescence agent		With coalescence agent‡	
	Time of coalescence (min.:sec.)	pH of serum	Time of coalescence (min.:sec.)	pH of serum
None (control)	50:00	4.50	0:40	4.51
Barium	4:25	4.10	0:40	4.21
Calcium	1:45	4.40	0:13	4.41
Lead	17:30	4.21	1:26	4.72
Magnesium	9:30	4.31	0:55	4.63
Zinc	17:00	4.06	3:00	4.23

\* Acetic acid coagulation run at 2% D.R.C. as follows: 300 cc. field latex, 4200 cc. dilution water, and 100 cc. 1% sodium soap (if used) added to latex and mixed, then 80 cc. of 2% acetic acid added. Salts when used were added to the acid prior to coagulation.

† Added as acetate (1% by weight on the rubber) dissolved in acetic acid coagulant.

‡ 1 part of coconut fat acids as sodium soap per 100 parts rubber by weight added to latex before coagulation.

the calcium especially so. In the presence of coconut oil soap, however, only the calcium ion shows enhanced activity.

*Calcium salts.*—As was shown in the preceding paragraph, the presence of calcium ions during coagulation with acetic acid speeds up the rate of coalescence of both the untreated fresh latex and identical latex containing coconut oil soap (1 per cent on the rubber). Broadly speaking, the effect where both agents are present appears to be additive. These data are given in Table VI.

TABLE VI  
EFFECT OF CALCIUM SALTS ON RATE OF COALESCENCE

Salt used	Percentage on rubber	Without coalescence agent		With coalescence agent	
		Coalescence (min.:sec.)	pH of serum*	Coalescence (min.:sec.)	pH of serum*
None	..	32:00	4.73	1:05	4.81
Calcium acetate	0.25	24:00	4.80	0:50	4.88
	0.50	18:00	4.86	0:31	4.90
	1.00	14:00	5.00	0:22	4.96
Calcium chloride	0.25	19:40	4.70	0:40	4.80
	0.50	14:23	4.70	0:35	4.80
	1.00	11:20	4.69	0:15	4.73

\* Within 1 hour of adding coagulant. Use of chloride has less effect on final pH of serum. Procedure of coagulation (at 2% D.R.C.) is the same as in Table V, but pH values of serum in Table VI series are higher than those in Table V series.

*Temperature.*—In an isolated experiment using 1 per cent stearic acid (added as the sodium soap) on the rubber as coalescence agent, coalescence occurred at 48° C in one-third to one-fourth the time required at 29° C when aliquots of identical latex were acidified with the same volume of acetic acid.

### COALESCENCE AGENTS

*Phenols.*—Certain phenols, notably *p*-chloro-*m*-cresol,  $\beta$ -naphthol, and pentachlorophenol, are just as active in promoting coalescence as is coconut oil soap (Table VII). They were dissolved as sodium salts in water before

TABLE VII  
USE OF PHENOLS\* AS COALESCENCE AGENTS

Agent used	Percentage on rubber	Without CaCl <sub>2</sub>		With CaCl <sub>2</sub> †	
		Coalescence (min.:sec.)	pH of serum	Coalescence (min.:sec.)	pH of serum
None	..	50:00	4.50	..	..
Soap‡	1	1:10	4.58	0:25	4.59
Quinosol	1	7:00	4.51	1:50	4.58
<i>p</i> -Chloro- <i>m</i> -cresol	1	1:00	4.60	0:25	4.69
<i>m</i> - and <i>p</i> -Cresol	1	4:55	4.64	1:15	4.68
$\beta$ -Naphthol	1	1:00	4.58	0:25	4.62
<i>p</i> -Chlorophenol	1	3:00	4.61	1:05	4.69
Pentachlorophenol	1	1:00	4.61	0:30	4.67
Resorcinol	1	13:00	4.61	3:00	4.65

\* Phenols as fungicides could be combined with soap as coalescence agents.

† 1% by weight of the rubber.

‡ Sodium soap of coconut oil fat acids.

addition to the fresh latex. As with the coconut oil soap, their activity is enhanced in the presence of calcium ion during coagulation. Small amounts of these active phenols could be mixed with the soap-treated latex to act in the capacities of preservative for latex and finished rubber, and coalescence agent during coagulation.

*Higher alcohols.*—Two of the higher alcohols, *n*-octyl and capryl alcohols, were found to be active in promoting coalescence at concentrations of 1 and

TABLE VIII  
OCTYL AND CAPRYL ALCOHOLS AS COALESCENCE AGENTS\*

Coalescence agent	Percentage on rubber	Coagulant per 100 grams of rubber		Time of coalescence (min.:sec.)	pH of serum
		10% sulfuric acid (cc.)	10% acetic acid (cc.)		
None	..	13.6	..	94:00	4.77
None	..	7.5	12.0	90:00	4.76
None	..	..	30.0	83:00	4.78
Crude lauric acid‡	1	16.0	..	0:60	4.75
Crude lauric acid	1	10.0	12.0	3:10	4.82
Crude lauric acid	1	..	36.0	1:45	4.72
Octyl alcohol‡	1	8.0	12.0	16:15	4.8
Octyl alcohol	2	8.0	12.0	8:30	4.8
Capryl alcohol‡	1	8.0	12.0	13:00	4.8
Capryl alcohol	2	8.0	12.0	1:35	4.8

\* Latex ammoniated to 0.2% NH<sub>3</sub> and aged 6 days before coagulation; coagulation run at 4% D.R.C.

† Crude lauric acid added to latex as sodium soap; coalescence accelerated control.

‡ Octyl and capryl alcohols were first emulsified separately in water, using 1% Aquarex-D (mostly sodium lauryl sulfate) on the alcohol, and thereafter added to the latex before acidification.

2 per cent on the rubber content of the latex. At 2 per cent concentration the capryl alcohol had activity comparable to that shown by lauric acid. In this instance the latex used was not fresh but had been aged 6 days in the presence of 0.2 per cent  $\text{NH}_3$ . Judging by the slowness of coagulation shown by this latex in the absence of added coalescence agents, it would seem that little if any hydrolysis of the fats or lipoids naturally present (with resulting ammonium soap formation) had occurred. Table VIII shows the results obtained.

#### RELATIVE ACTIVITY OF FATTY ACIDS

Coalescence activity of an homologous series of saturated straight-chain fatty acids was investigated. The results, although fragmentary because of lack of material, are extremely interesting. The data set forth in Table IX are plotted in Figure 1 as time of coalescence (activity) against number of

TABLE IX  
SATURATED STRAIGHT-CHAIN FATTY ACIDS AS COALESCENCE AGENTS\*

Fatty acid	Quantity† per 100 grams of rubber	Time of coalescence (min.:sec.)
Formic	0.5	36:00
Acetic	0.6	39:00
Propionic	0.7	31:20
Butyric	0.9	25:00
Valeric	1.0	29:00
Caproic	1.2	24:00
Heptanoic	1.3	10:00
Capric	1.7	0:12
Lauric	2.0	0:15
Palmitic	2.6	2:30
Stearic	2.8	13:30

\* Coagulation at 2% D.R.C. with 2% aqueous acetic acid at pH 4.6-4.8.

† Coalescence agent added to latex before coagulation, in 0.01 molar quantities on 100 grams of rubber, dissolved in a minimum of aqueous ammonia.

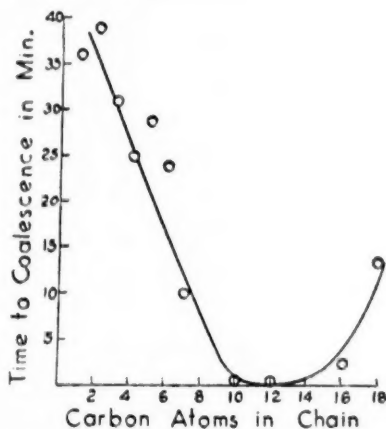


FIG. 1.—Effect of number of carbon atoms in chain on activity of saturated straight-chain fatty acids as coalescence agents.

carbon atoms in the chain. There is a progressive increase in activity as chain length increases to 10 or 12 carbon atoms, and a decrease in activity as the

number rises beyond this point. This peak of activity in the region of 10 to 12 carbon atoms calls to mind instances of such an effect encountered in other investigations—for example, that of Smith and Boone<sup>15</sup>, who compounded this same series of fatty acids in a vulcanizable rubber stock. Tensile strengths for the vulcanized rubber rose to a maximum as the fatty-acid chain length increased to the region of about 10 carbon atoms and thereafter gradually declined. Below this point the acids containing an odd number of carbon atoms in their chains showed highest activation effect; above this point the even-numbered chains assumed pre-eminence.

Translating this into practice from the standpoint of adequate coalescence activity as well as of low cost, the use of coconut oil soap for latex pretreatment is clearly indicated.

#### EFFECT OF DRY RUBBER CONTENT OF LATEX

*On rate of coalescence.*—The change in rate of coagulation (in the presence of coalescence accelerators) as the latex is diluted from about 25 per cent D.R.C. down to 2 per cent is not so striking as might be imagined. Although the time is halved at the higher concentration, coagulation in no case in this series required so much as 60 seconds (Table X). The real difference, practically

TABLE X  
EFFECT OF D.R.C.\* OF LATEX AT COAGULATION  
OF RATE OF COALESCENCE†

D.R.C. of latex at coagulation (%)	Volume of reagents (cc. per plan)				Time of coalescence (min.:sec.)	pH of serum
	Latex	Soap	Water	Acid		
1.8	300	100	6000	80	0:40	4.79
1.8	300	100	6000	80	0:40	4.77
2.6	300	100	4025	80	0:30	4.82
2.6	300	100	4025	80	0:34	4.83
5.4	300	100	1685	80	0:25	4.58
5.4	300	100	1685	80	0:27	4.60
8.5	300	100	905	80	0:35	4.70
8.5	300	100	905	80	0:25	4.69
11.7	300	100	515	80	0:42	4.55
11.7	300	100	515	80	0:35	4.54
15.6	300	100	271	80	0:25	4.59
15.6	300	100	271	80	0:30	4.53
19.3	300	100	125	80	0:25	4.60
19.3	300	100	125	80	0:20	4.51
23.7	300	100	15	80	0:24	4.52
23.7	300	100	15	80	0:20	4.50
2.0	Control, no coalescence agent				42:00	4.73

\* Dry rubber content of latex as received, 39.04%.

† Coalescence accelerator, sodium soap of coconut fat acids added as a 1% aqueous solution to the latex; coagulant, acetic acid added as 2% aqueous solution.

speaking, is not in the time but rather in the strength of the clots; those made at the higher concentrations were much stronger and easier to handle during machining.

*On acetone extract.*—The fat acids used as coalescence accelerators (and added as soaps in the latex pretreatment) reappear in the acetone extract of the rubber after the drying of the sheet. The acetone extract of such rubber (continuous sheet rubber, C.S.R.) is higher than that of the controls (thin sheet rubber, T.S.R., and standard crepe), and the free fat acid content of such rubber is also higher; but the fat acids are not recovered quantitatively (Table XI).

TABLE XI  
EFFECT OF ADDED FAT ACIDS ON ACETONE EXTRACT

Rubber type	D.R.C. at coagulation (%)	Fat acid used	Acetone extract		Added fat acid retained (%)
			Per cent	Mg. KOH per 100 grams of rubber*	
Latex L-499 + 0.2% NH <sub>3</sub> , coagulated with acetic acid 3 days after being received					
T.S.R. washed	2	None	{ 2.10 2.09 }	{ 175 176 }	Control
C.S.R. washed	2	1% coconut (calcd. as lauric)	{ 2.75 2.74 }	{ 336 330 }	57
C.R.S. washed	2	1% C.P. capric	{ 2.53 2.56 }	{ 280 278 }	32
Latex L-500 coagulated with acetic acid same day as received					
T.S.R. washed	2	None	{ 2.02 2.02 }	{ 79 81 }	Control
C.S.R. washed	2	1% coconut (calcd. as lauric)	{ Flask broke 2.83 }	{ . . . 294 }	76
Pale crepe	15	None	{ 2.16 2.23 }	{ 74 72 }	Control

\* Acetone extract dissolved in 20 cc. of methyl alcohol and titrated with 0.084 N KOH, using phenolphthalein indicator; 1 cc. of 0.084 N KOH required to neutralize acid in blank containing 20 cc. of methyl alcohol.

In the case of coconut fat acids (calculated as lauric acid) only about 50 to 75 per cent of the added fat acid (compared with the control) is retained by the rubber. In the case of capric acid, only one-third of the added amount was retained. Although the particular sheets described here received a special washing treatment in water, the loss of fat acid is not more significant than that experienced in the standard practice of washing a coagulum on a mill in the making of pale crepe, as will be seen on comparison of the acid number of T.S.R. and pale crepe controls made from latex L-500.

#### ACTION OF COALESCENCE ACCELERATORS ON CENTRIFUGE CONCENTRATES

Centrifuged concentrates (1 day old and containing 0.16 per cent NH<sub>3</sub>) responded normally to coconut oil soap as coalescence agent. A limited number of trials with the skim fractions (using 1 per cent coconut oil soap, based on the D.R.C. followed by acidification to pH 4.8 to 4.9) produced flocculated mixtures rather than a continuous sheet. At the time, there was no particular reason to do further work with the skim fraction. It may be that intensified

effort and the use of very active agents, such as ricinoleic acid, in higher concentrations could convert centrifugal skim into continuous sheet by this process.

### THEORY OF COAGULATION

As a result of these experiments and a general experience with coagulation of Hevea latex, the conclusion is reached that the essential feature of clot formation is fusion of the latex particles in a manner entirely analogous to the adhesion of two clean surfaces of unvulcanized rubber. [The experiments of Seifriz<sup>16</sup> with Hevea and *Cryptostegia* latex led him to the same or essentially the same conclusion.] As in the latter case it would not seem essential that the surfaces be completely clean to permit at least spotty fusion, but it would follow that, other factors being constant, the more complete the fusion, the stronger the clot would be.

In the ionic type of coagulation the important factors are believed to be: (1) neutralization of the electric charge on the surface of the particle<sup>17</sup>; (2) dehydration of adsorbed surface layer<sup>17</sup>; (3) clearing of the surface of the particle; and (4) fusion of the latex particles.

This is regarded as the sequence of events in the case of acetic acid coagulation of fresh latex. As the dehydration (2) and clearing of the surface (3) are time factors, the induction period preceding coalescence would be of appreciable duration, as is found in actual practice.

The function of coalescence agents is regarded as primarily that of clearing the surface of the particle by preferential adsorption. When, for example, soap is added to fresh latex, displacement of adsorbed serum material occurs because of adsorption of the soap molecules. On acidification, the soap molecules are converted into rubber-soluble fat acids. This function of cleaning the surface of the latex particles here ascribed to the coalescence agent, although arrived at independently, is essentially that of the enzyme rennet in the coagulation of milk as viewed by Schryver<sup>18</sup> in his studies thirty-odd years ago.

The absence of coalescence phenomena when either Barrowcliff latex or B liquid are acidified can be clarified by assuming that the heat treatment (to which these latices are subjected during preparation) coagulates the adsorbed serum material on the surface of the latex particles. This in effect encloses each particle in an envelope. When acidified, such latices do not coalesce because the surfaces of the particles are not clean. Addition of the coalescence agent by preferential adsorption displaces this film, and, on acidification under such conditions, coalescence ensues. It need not be assumed, as was mentioned before, that the particle surfaces be completely cleared.

Coalescence of Barrowcliff latex and B liquid can also be induced by the introduction of relatively small amounts of fresh latex. Van Harpen<sup>19</sup> calculates that the ratio of the rubber in fresh latex to that of the rubber in B liquid is in the range of 1:2000 to 1:20,000. At first sight it is difficult to see how such small amounts can be effective. However, if the matter is viewed from the standpoint of surface area or the number of fresh latex particles added during the inoculation, the case becomes more undesirable. Hauser<sup>20</sup>, using Henri's data<sup>21</sup>, calculates that there are about 200,000,000 particles in 1 cc. of latex of 35 per cent D.R.C. (This value, determined before the advent of ultraviolet and electron microscopy, is probably low.) An ordinary drop (0.05 cc.) should, therefore, carry at least 10,000,000 particles as well as an undetermined number of microorganisms. The inoculation technique could there-



fore induce coalescence in Barrowcliff latex or B liquid by an entrapping action in which the added fresh latex coagulates after acidification and the resulting network encloses the particles of B liquid forming a weak coagulum. (Micro-organisms, introduced in the fresh latex droplets used in the inoculation of B liquid, can conceivably, through fermentative action, clear a portion of the surface of the rubber particles in the B liquid. This would increase the chances for fusion into a clot.)

In the case of coagulation of latex by pressure, as by rubbing a drop between the fingers, only points (3) and (4) appear involved. Pressure overcomes the repulsion set up by electric surface charges, forces a displacement of the adsorbed serum material—in effect clearing the surfaces of the latex particle—and forces fusion of the particles into a clot.

#### CONTINUOUS SHEET RUBBER PRODUCTION

An arrangement for the continuous processing of field latex into sheet rubber appears to offer the advantages of improved uniformity of product and reduction in factory floor space for a given output of rubber. These apparent advantages may become real in the case of large block estates preferring to use a central factory, or in case of the amalgamation of the latex output of smaller estates; the latter method has been suggested from time to time, as, for example, by Ascoli<sup>22</sup>.

In dealing with the problem of continuous production of sheet rubber from Hevea latex, at least six points arise for consideration. These are: (1) continuous feeding of streams of latex and coagulant in proper proportions; (2) control of the induction period preceding coagulation by accelerating the rate of coalescence of the flocculated rubber particles; (3) formation of the coagulating latex into a ribbon and means of its transportation to the sheeting battery; (4) continuous machining of the ribbon into wet sheet; (5) drying the wet sheet; and (6) packing the dried rubber.

*Continuous feed.*—Once the idea presents itself of continuously feeding latex and coagulant into a containing vessel to form a ribbon of coagulum, the actual proportioning of the liquids offers no real difficulty. An acceptable method is the use of rotameters, one for the latex and one for the coagulant stream, fed from bulking tanks by gravity or under low air pressure. The outlets should be arranged to set up turbulent flow to ensure adequate mixing of the coagulant with the latex.

*Control of induction period.*—This step, in company with continuous feed, is essential to the success of the method. Control of coagulation rate is accomplished by addition of coalescence agents to the latex before its admixture with coagulant, as has been described in foregoing sections of the discussion. It is entirely possible to obtain adequate acceleration of coagulation by addition of the coalescence agent to the acidified latex, but pretreatment of the field latex is the preferred and simpler method. Also preferred is the adjustment of the rate to give a firm coagulum in about 1 minute after admixture of the treated latex and coagulant. For general-purpose rubber, this rate may be obtained by the addition to the field latex of 1 per cent of coconut oil soap alone or together with a smaller amount of one of the phenolic materials (Table VII) as a fungicide. Although the coagulation may be made instantaneous, as by the use of ricinoleic acid (Table II), it is not desirable to do so because of the difficulty then encountered of uniformly mixing in the coagulant.

*Experimental machine.*—The simplest method of forming the coagulum into a continuous ribbon is to flow the coagulating latex mixture down a trough,

but this is not a positive method. There is a tendency for the flocculated latex and the freshly set coagulum to adhere to the sides of the trough and cause undesirable accretions which impede smooth flow. This is especially true in cases where coagulation is run with low D.R.C. latex. The difficulty may be minimized by keeping the sides of the trough wet with water or by lining the trough with a very smooth surface which is readily wetted by water.

The best method, however, is to run the coagulation on a horizontally moving conveyor belt (Figure 2). The outside surface of an endless conveyor

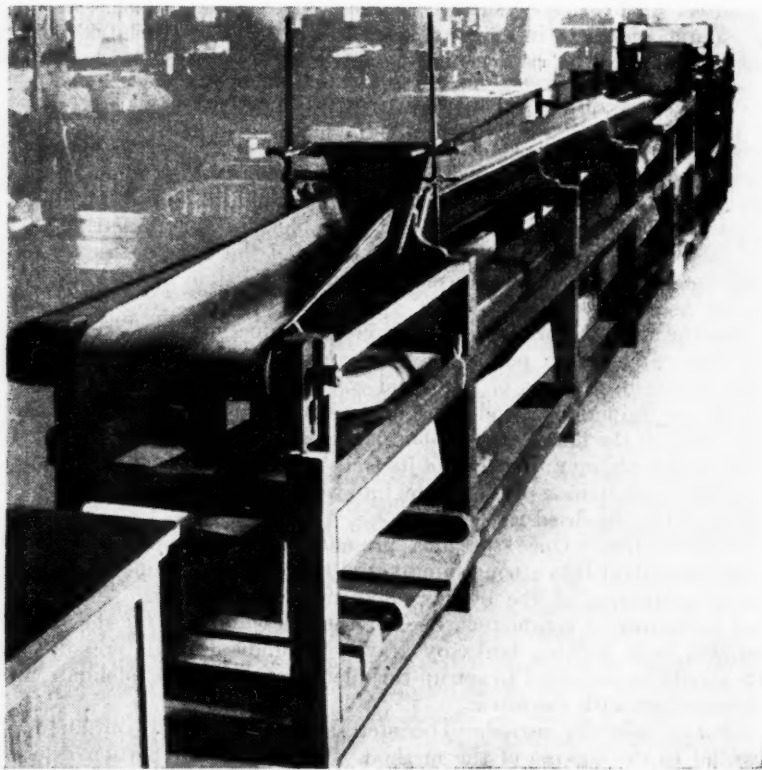


Fig. 2.—Continuous sheet rubber machine with coagulum conveyer trough in foreground.

belt (about 8 inches wide in this case) is covered with a flexible sheet of vulcanized rubber which projects 5 or 6 inches beyond the edges of the conveyor belt. At the ends of the machine this special belt moves flat over driven rolls, and from there is passed down a trough having sloping sides. When the belt enters the trough section, the rubber flanges are bent upward to form a moving rubber lining. One end of this trough section is sealed by a thin rubber sac shaped to the cross-section of the trough. Contact with the sides of the trough is maintained by inflating the sac with air or with a liquid, such as calcium chloride brine. The sac is prevented from bulging under inflation pressure by flat metal plates on either side. Alternately, the seal may be made by feeding the conveyor belt into the trough section at an angle. This particular machine

had a trough section about 12 feet long, and the belt moved at the rate of 6 feet per minute. For large scale production this rate would be increased several times.

In operation, a movable dam was placed in the trough section just beyond the rubber sac. Streams of treated latex and coagulant were proportioned into

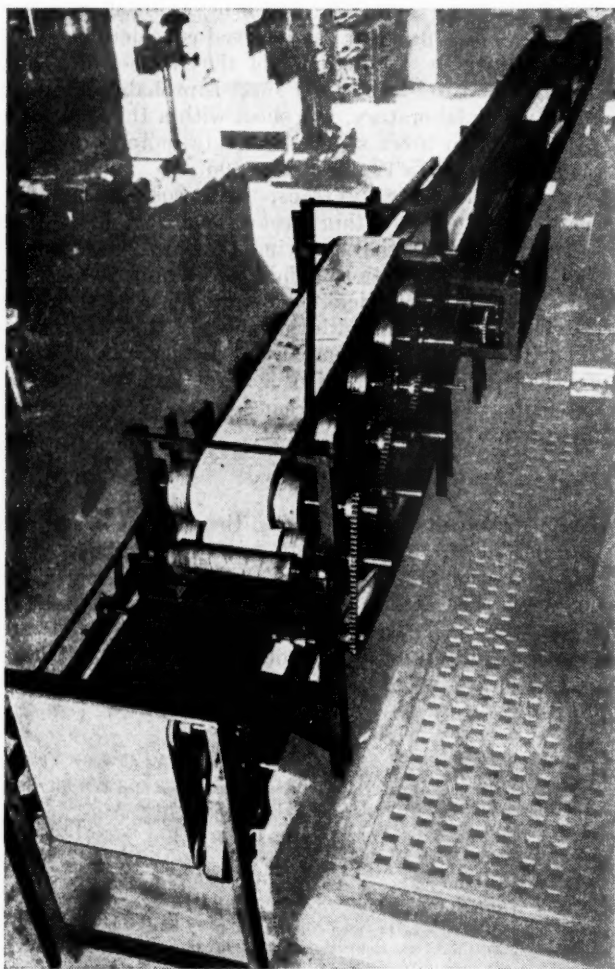


Fig. 3.—Continuous sheet rubber machine with sheeting battery in foreground.

the space so formed. When the space was filled to the depth required, the machine was started. After a travel of about 6 feet the latex first added began to coagulate. This solid coagulum formed the seal at the exit end of the trough; at that time the removable dam, no longer required, could be lifted out, and a continuous ribbon of coagulum emerged.

*Machining the coagulum.*—This ribbon of coagulum was fed into a continuous sheeting battery where excess serum was squeezed out. Figure 3 shows

the battery actually used in the experimental machine. The continuous ribbon of coagulum was gradually squeezed between two cloth-covered conveyor belts supported by a series of rolls. This type of compressing machine was used because of interest in coagulation of latex at high dilution. Continuous sheeting batteries were commercially available before the war and doubtless could be adapted to handle this type of coagulum when made from latex of about 15 to 25 per cent D.R.C.

*Drying wet sheet.*—This problem has received considerable attention in the past, and more recently by Piddlesden<sup>23</sup> of the Rubber Research Institute. Continuous drying of natural-rubber wet sheet is probably feasible if the sheet is thin enough. In this laboratory, wet sheet with a thickness of about 0.015 inch, made by a filtration process and seemingly more porous than machine coagula, has been dried in 8 to 12 minutes at 105° C. The method of continuously preparing and mechanically transporting coagula as here described is ideally suited to the handling of thin sheet as feed stock for continuous driers.

*Packing.*—This matter, like that of drying wet sheet, has in the past received more than a modicum of attention. Thin sheet prepared by a continuous method could be rolled into cylinders, or, better (for stacking), folded and cut into rectangular blocks, as is done with thin sheet at the synthetic rubber plant designed by The B. F. Goodrich Company at Louisville. There seems to be merit in the idea of preparing parcels of a shape and size that can be easily handled by one man. This is the experience of the synthetic rubber industry and of manufacturers who use that product.

### SUMMARY

Quantitative experiments in controlling the rate of coagulation of fresh Hevea latex are described, and the results have been applied in a process for the continuous preparation of sheet rubber on a laboratory scale. As with most continuous processes, this method is more applicable where large, rather than small, volumes of latex must be worked up. Its apparent advantages reside in a possible improvement in uniformity of product and a reduction in factory floor space for a given output of rubber.

### REFERENCES

- <sup>1</sup> Biffen, *Ann. Botany* **12**, 165 (1898).
- <sup>2</sup> Stevens, *Bull. Rubber Growers' Assoc.* **21**, 404 (1939).
- <sup>3</sup> Wingfoot Corp., Straits Settlements Reg. No. 717 (patent application filed Feb. 19, 1937); Stewart and Newton, U. S. patent 2,304,858 (Dec. 15, 1942); British patent 537,645 (July 1, 1941).
- <sup>4</sup> Calcott and Starkweather, U. S. patent 2,187,146 (Jan. 16, 1940); Semon, U. S. patent 2,366,460 (Jan. 2, 1945); Wanderer, U. S. patent 2,371,722 (Mar. 20, 1945).
- <sup>5</sup> Willson, E. A., unpublished work.
- <sup>6</sup> Whithy, *Orig. Com. 8th Intern. Congr. Applied Chem.* (Appendix) 25, 597 (1912).
- <sup>7</sup> De Vries, *Rec. trav. chim.* **62**, 701 (1923).
- <sup>8</sup> Eaton and Grantham, *Agr. Bull. Federated Malay States* **4**, 426 (1915).
- <sup>9</sup> Barrowcliff, *J. Soc. Chem. Ind.* **37**, 49 (1918).
- <sup>10</sup> Campbell, *Caoutchouc and Gutta-percha* **14**, 9243 (1917).
- <sup>11</sup> De Vries and Beumée-Nieuwland, *Arch. Rubbercultuur* **9**, 726 (1924).
- <sup>12</sup> De Vries and Beumée-Nieuwland, *Arch. Rubbercultuur* **11**, 530 (1927).
- <sup>13</sup> Boil 9 volumes of water, add 1 volume of fresh latex, boil 3 minutes, hold at 100° C for 5 minutes, then cool to room temperature. The product is similar to Barrowcliff latex in reaction to acid and to inoculation with fresh latex.
- <sup>14</sup> Van Harpen, "Electrometric Determination of Hydrogen Ion Concentration in Latex of Hevea Brasiliensis and its Applicability to Technical Problems", Varecamp & Co., Medan, 1930, p. 258.
- <sup>15</sup> Smith and Boone, *Ind. Eng. Chem.* **19**, 398 (1927).
- <sup>16</sup> Seifriz, *Science* **102**, 378 (1945).
- <sup>17</sup> Kruyt and Van Klooster, "Colloids", New York, 1927, pp. 109 and 185.
- <sup>18</sup> Schryver, *Proc. Roy. Soc. (London)* **B86**, 460 (1913).
- <sup>19</sup> Van Harpen, "Electrometric Determination of Hydrogen Ion Concentration in Latex of Hevea Brasiliensis and its Applicability to Technical Problems", Varecamp & Co., Medan, 1930, p. 261.
- <sup>20</sup> Hauser, "Latex", Th. Steinkopff, Leipzig, 1927, p. 56.
- <sup>21</sup> Henri, *Caoutchouc and Gutta-percha* **3**, 511 (1906).
- <sup>22</sup> Ascoli, *Trans. Inst. Rubber Ind.* **21**, 225 (1945).
- <sup>23</sup> Piddlesden, *J. Rubber Research Inst. Malaya* **7**, 117 (1937).

# CHEMICAL CHANGES IN AMMONIATED HEVEA LATEX\*

R. F. A. ALTMAN

52H, LAAN VAN MEERDERVOORT, THE HAGUE, HOLLAND

As generally accepted, the preservative action of ammonia on latex is due to the neutralization of the acids formed from certain latex components by bacteria or enzymes and to its inhibiting action on bacterial growth. The chemical composition of latex undoubtedly changes on ammoniation as different components, probably including the rubber itself<sup>1</sup>, are chemically affected by the alkaline action of ammonia. So far, only little insight has been obtained into the chemistry of these changes. In this connection reference should be made to the work of Rhodes<sup>2</sup>, who systematically followed the changes in various characteristics of the latex over a period of fourteen months. The averages of the figures obtained by Rhodes are recorded in Table 1. The

TABLE 1  
MEANS FOR VARIOUS LATEX CHARACTERISTICS (RHODES)

Latex characteristics	Fresh latex before ammoniation	Freshly ammoniated latex	Latex after 10 days' ammoniation	Latex after 50 days' ammoniation
Dry rubber content (per cent)	37.65	—	36.17	—
Total solids (per cent)	40.12	—	39.14	—
Non-rubbers (per cent)	2.47	—	2.97	—
Acetone extract (per cent)	3.41	3.36	3.84	3.91
Acid value of acetone extract in mg. KOH per 100 g. of whole latex rubber	139	118	256	299
Surface tension (dynes)	44.7	—	38.6	37.8
Viscosity (centipoises)	15.3	—	5.6	5.3

reader is referred to the original paper for the interesting comments made on these figures.

In the present publication the changes in the nonrubber ether-soluble part of the latex have been followed analytically over a fifteen months' period. The experiments were conducted in such a way that, at certain time intervals, samples of 100 cc. were taken from the vigorously shaken bulk of latex which had been ammoniated immediately on arrival in the laboratory. Exclusively latex of clone Tjirandji 1 from the Experimental Garden Tjiomas near Buitenzorg, Java, was gathered for this purpose.

The author has already described the preparation of the ether-solubles from latex, as well as the estimation of the yield, acid number and saponification value of the ether-solubles<sup>3</sup>. The organic-acid content and the content of the unsaponifiable substances were determined according to the method of Fahrion<sup>4</sup>, which had to be modified for semi-microanalytical purposes, since from the one gram of ether-solubles about 0.3 gram was required for the determination of the

\* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 22, No. 6, pages 302-307, April 1947.



acid and saponification values. In determining the unsaponifiables, the ether-soluble sterols were removed as far as possible.

### EXPERIMENTAL

The experimental results obtained are summarized in Table 2 and plotted in Figures 1-4. The following comments should be read in conjunction with the author's previous paper<sup>3</sup>.

TABLE 2  
CHEMICAL CHANGES IN AMMONIATED HEVEA LATEX

Time of ammoniation	Yield of ether- solubles in g. per 100 cc. latex	Acid value in mg. KOH per g. ether- solubles	Saponif. value in mg. KOH per g. ether- solubles	Organic acids		Unsaponifiables	
				In % of ether- solubles	In g. per 100 cc. latex	In % of ether- solubles	In g. per 100 cc. latex
0 (before amm.)	1.0062	32.2	146.6	60.1	0.6050	22.7	0.2284
1-3 min. (freshly amm.)	1.0080	28.7	147.6	58.1	0.5857	19.6	0.1980
1 hour	0.9286	17.1	145.4	59.4	0.5512	20.1	0.1874
6 hours	0.9171	20.2	142.6	60.6	0.5559	20.9	0.1922
24 hours	0.9168	32.4	128.4	61.6	0.5651	20.2	0.1837
2 days	0.9163	38.7	127.0	62.0	0.5686	25.3	0.2351
1 week	0.9001	62.6	121.5	67.3	0.6059	23.1	0.2081
1 month	0.8192	98.0	126.4	74.2	0.6079	24.4	0.1995
2 months	0.7831	103.2	143.1	70.4	0.5514	31.9	0.2500
3 months	0.7459	105.8	149.1	67.8	0.5054	28.8	0.2148
15 months	0.6935	113.8	134.4	69.4	0.4813	29.0	0.2011

The change in yield is expected, as the saponifiable components of the ether-solubles, on hydrolyzing, produce certain compounds which do not dissolve in ether and therefore are not included in the samples for analysis. Theoretically speaking, the decrease in yield continues as long as hydrolysis progresses, and reaches a constant value when saponification is completed. From the experimental data it is clear that the yield of ether-solubles decreases, at first somewhat rapidly, and is not complete at the end of fifteen months. Other factors possibly influencing the yield are: (1) the oxidative cleavage of unsaturated fat acids taking place one or more months after ammoniation (see below, the change in saponification value); (2) the formation of a deposit<sup>5</sup> on the bottom of the latex container, which even after vigorous stirring could not be emulsified completely in the latex, thus being partly excluded from the samples of analysis. The change in acid value may be explained as follows. The rapid decrease in the first hour of ammoniation must be due to the immediate transformation of all free acids present in the latex into their ether-insoluble magnesium and calcium salts. The same holds true for the ammonium salts of the fat acids, because the corresponding calcium and magnesium salts are insoluble in water or latex serum. Due to the saponification processes always taking place in executing the adopted method of analysis, an acid value of about 20 is regularly found instead of a value of 0.

The sharp rise in the acid value must be due to: (1) the increasing amount of fat acids formed by the gradually saponifying fats and phospholipids, and (2) the increasing amount of phosphoric acid, which is derived from the phospholipids and which liberates the ether-soluble fat acids from their magnesium and calcium salts mentioned earlier. It will be understood that ammonium phosphate as well as free phosphoric acid react with the calcium and especially with



the magnesium salts of the fat acids, producing water- and ether-insoluble phosphates.

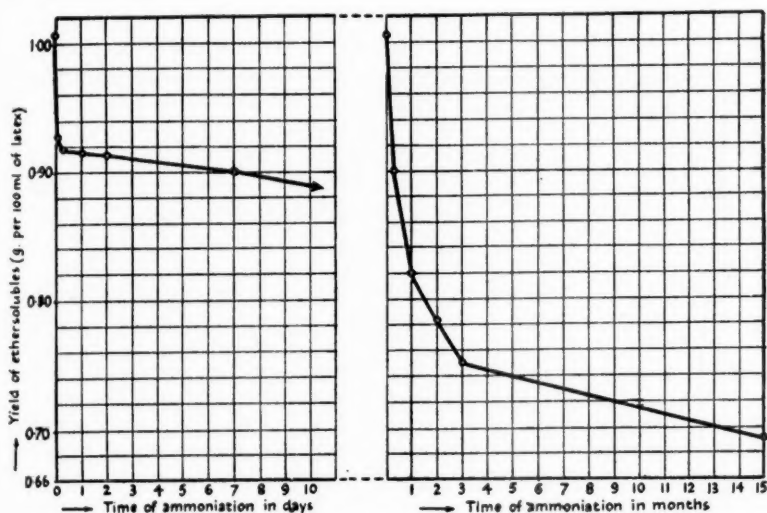


FIG. 1

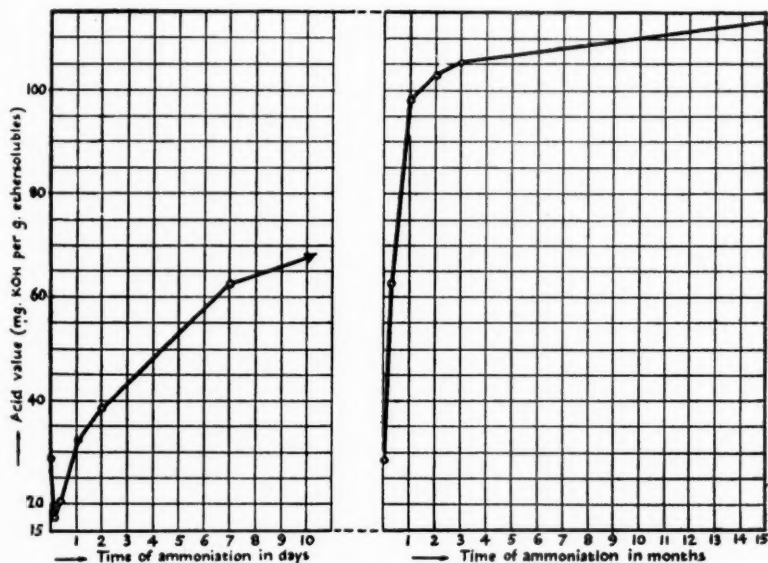


FIG. 2

It should be remarked that the fat acids, although occurring in ammoniated latex as their ammonium salts, are quantitatively estimated by this method of analysis. The ammonium soaps are very soluble in the boiling diluted alcohol

applied in the extraction procedure, and may be considered to be completely hydrolyzed in the aqueous solution obtained as a result of the alcohol evaporation *in vacuo*. The aqueous solution therefore, contains the free fat acids which are quantitatively extractable by ether.

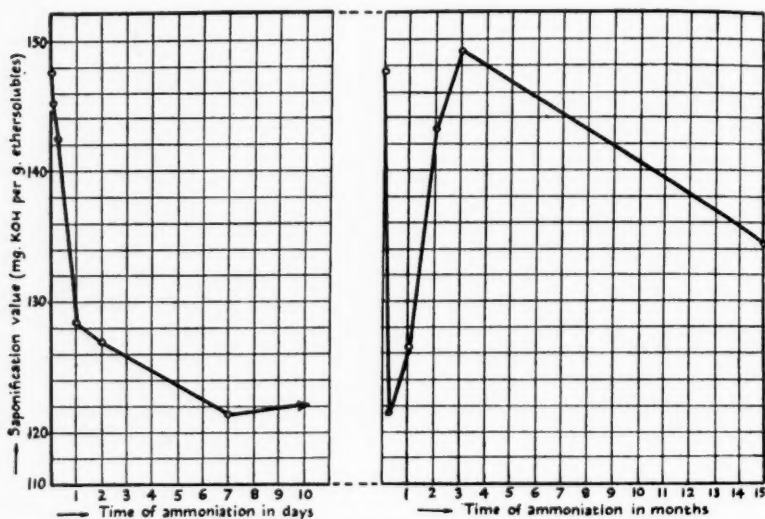


FIG. 3

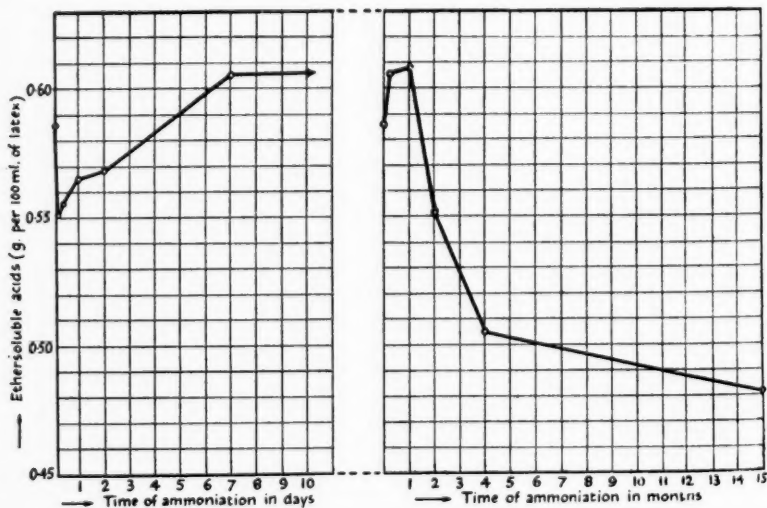


FIG. 4

The change in the saponification value is most interesting. The marked decrease during the first few days is expected, as phospholipids, on hydrolyzing,

give strongly decreasing saponification values<sup>3</sup>. Theoretically speaking, this decrease should continue as long as hydrolysis of the phospholipids takes place. In practice, however, saponification values pass through a minimum and then increase to a sharp maximum, followed by a slow decrease. An explanation of this unexpected fat may be found in the gradually formed phosphoric acid, liberating the fat and other ether-soluble acids from their magnesium and calcium salts. In other words two factors influence the saponification value, one which decreases, the other which increases it. The curve obviously reaches its maximum height as soon as all ether-soluble acids are liberated from their salts. A possible formation of acids by bacterial action, such as may be the case in spontaneously coagulating latex<sup>3</sup>, has to be excluded in ammonia-preserved latex.

The final slow decrease in the saponification value is probably due to the already progressed spontaneous oxidation of the unsaturated fat acids forming a mixture of aldehydes, ketones, lactones, oxy and hydroxy acids, and other acids of smaller molecular weight than those originally present, as well as alcohols, carbon dioxide, and moisture<sup>6</sup>. Moreover, unsaturated acids can form ether-insoluble polymerization products.

The change in the organic acid content calls for the following comment. Theoretical considerations lead to the expectation that the amount of ether-soluble organic acids, first of all, must decrease because of the formation of ether-insoluble magnesium and calcium salts, and afterwards must increase as soon as the fat acids gradually formed by the saponifying fats and phospholipids find no more calcium and magnesium-ions available. Another factor increasing the amount of the ether-soluble acids may be found in the phosphoric acid and its glycerol esters, which liberate the organic acids from their salts.

The experimental results agree with the above explanation, except that the quantity of organic acids decreases again in the second and following months of storage. The author is inclined to attribute this last fact to the oxidative decomposition of the unsaturated fat acids.

*Change in the content of unsaponifiable matter.*—Except for two irregular results, no change in the content of the unsaponifiable matter took place during the fifteen months of storage. This is in complete agreement with the theory.

#### ADDITIONAL REMARKS

It appears from the acid and saponification values that, even after fifteen months' storage, the ether-solubles of ammoniated latex still contain unhydrolyzed saponifiable compounds. This striking fact is probably due to the presence of waxes and sterol esters, which are known to be stable against chemical saponification agents such as ammonia.

In this connection it can be seen from Table 2 that, after one month's storage, the sum of the organic acids and of the unsaponifiable matter, expressed as percentages, amounts almost to 100. Confusing conclusions may be drawn from this calculation, indicating that saponification should, indeed, be completed after one or two months. As a matter of fact, however, the ether-solubles on saponifying absorb, relatively speaking, considerable amounts of water, so that, when the sum of percentages amounts to 100, this does not signify that all fats, phospholipids, waxes, etc., are completely saponified.

Attention may be finally drawn to the fact that the experimental results obtained by Rhodes<sup>2</sup> can easily be explained by the considerations given above.

## ACKNOWLEDGMENT

The writer is indebted to P. Honig, Director of the Rubber Research Institute at Buitenzorg, Java, for permission to publish the paper, and to H. R. Braak and P. Honig for assistance in revising the manuscript.

Valuable assistance in the experimental work by Djûpri is gratefully acknowledged.

## REFERENCES

- <sup>1</sup> Kemp and Peters, *Ind. Eng. Chem.* **33**, 1391 (1941).
- <sup>2</sup> Rhodes, *India-Rubber J.* **97**, 82 (1939).
- <sup>3</sup> Altman, *Trans. Inst. Rubber Ind.* **22**, 274 (1947).
- <sup>4</sup> Fahrion, in Klein, "Handbuch der Pflanzenanalyse", Vienna, 1932, Vol. 2, p. 630.
- <sup>5</sup> De Vries, *Arch. Rubbercultuur* **7**, 168, 186, 193 (1923); **9**, 345, 694 (1925); **10**, 149 (1926); **11**, 289, 325 (1927); Martin, *Trans. Inst. Rubber Ind.* **2**, 354 (1927).

## THE THERMOPLASTICITY OF THERMOPRENE. A STUDY OF THE ADHESION OF RUBBER TO METAL \*

ANDRÉ JARRIJON AND PIERRE LOUÏA

INSTITUT FRANÇAIS DU CAOUTCHOUC, PARIS, FRANCE

89, 325

### INTRODUCTION

Among chemical derivatives of rubber, there is a type to which has been given the name of *isorubbers* or *cyclorubbers* in the technical literature. Kirchhof<sup>1</sup> has described at length these products, which can be prepared by various methods, *e.g.*, by the action of heat, as described by Harries<sup>2</sup>, who isolated a white amorphous powder, having a density of 0.992, by heating rubber for several hours in ether at 250–300°, under pressure, or by the action of chemical reagents, particularly sulfuric acid and inorganic and organic halogenated compounds, with which a range of products suitable for molding powders, paints, sheets, wire, etc., can be prepared.

The present work is concerned, not with a further study of these products, but rather with an investigation of a particular one of these products, *viz.*, that which is obtained by treating rubber with phenolsulfonic acid. The B. F. Goodrich Company, and Fisher<sup>3</sup> in particular, have successfully developed the manufacture and use of this product, and have given it the generic and commercial name of Thermoprene. At the beginning, a large number of applications of Thermoprene were foreseen, but only one application has survived and undergone any extensive development, *viz.*, the use of Thermoprene as an adhesive for bonding rubber to metal, a process known as the Vulcalock process.

As a result of newly observed facts, it seemed of interest to take up this problem again in an attempt to improve the process in certain ways.

In the Vulcalock process of adhesion, the first step is to prepare a hard resin (called Phenolac or Thermoprene S. L.) by the action of phenolsulfonic acid on crude rubber when hot. The process, which is extremely simple, is carried out in two steps; the first involves adding a small proportion of phenolsulfonic acid to crude rubber on a mixing mill; then, as a second step, heating the mixture for several hours at 135° C. In this way a hard, brittle, thermoplastic mass is obtained, which is readily dissolved in any of the ordinary solvents of rubber. Such a solution of the product, when spread on the sanded surface of a metal, imparts good adhesion to rubber mixtures subsequently vulcanized in contact with the surface.

However, in spite of the fact that excellent bonds are obtained, they have the serious shortcoming that the bonding agent is thermoplastic. Even after being vulcanized, the product becomes soft above 70° C, and unfortunately this means that the bonds give way above this temperature.

The present authors have attempted to utilize reactions discovered at the French Rubber Institute to overcome this disadvantage. It will be shown that,

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from the *Revue Générale du Caoutchouc*, Vol. 22, No. 1, pages 3–5, January 1945.

even if the results obtained are not of direct importance at the moment, they throw light on the reactions of phenolsulfonic acid with rubber. At the same time they indicate that the remarkable adhesion obtained with this type of product may depend on the presence of phenolsulfonic groups fixed on the rubber molecule. Like the chlorine in chlorinated rubber, then, the sulfonic group imparts a great affinity for metals.

#### ACTION OF PHENOLSULFONIC ACID ON RUBBER MODIFIED BY MALEIC ANHYDRIDE

Compagnon and Le Bras<sup>4</sup> have studied the reaction of rubber with maleic anhydride when carried out on a mixing mill, and have shown that one of the characteristic properties of this modified rubber is that it is less thermoplastic than ordinary rubber. It is this particular property of modified rubber which it seemed desirable to take advantage of. It was, in fact, thought that it might be possible, by the action of phenolsulfonic acid on rubber whose plasticity had been reduced, to obtain a product the thermoplasticity of which might be correspondingly less. This view was actually substantiated experimentally. Phenolsulfonic acid can be easily incorporated into modified rubber on a mill in the same way as is done with ordinary rubber. When the resulting mixtures are heated, the reaction takes place without any particularly unusual phenomenon except that the mass, instead of becoming doughy and sticky, remains dry. When cold it is friable and can be very easily pulverized, especially when it is worked on a washing mill in the presence of water. This powder retains considerable thermoplasticity, and this property makes it possible to sheet it out on a heated mill into sheets of any thickness, which are very smooth and very stiff. The reduction in thermoplasticity compared to that of ordinary rubber depends on the percentage of maleic anhydride incorporated in the rubber, *i.e.*, the higher the percentage of maleic anhydride, the greater the degree to which the thermoplasticity of the product is reduced. It would appear, therefore, that the desired effect is attained in this way. In reality however, two important disadvantages were found; first the difficulty of dissolving these less thermoplastic products and, secondly, their relatively poor bonding properties. The derivative prepared from ordinary rubber can be dissolved very easily provided that the precaution is first taken to masticate it for a long time, *e.g.*, for one hour on a hot mill. Its solutions are then quite stable. On the contrary, rubber which has reacted with maleic anhydride forms a mass which cannot be rendered soluble simply by milling, and it is necessary to incorporate into the mass relatively large percentages of products which are capable of facilitating its solution. In this category Arubren<sup>5</sup> has given good results. Nevertheless, even with this aid, the solutions obtained are not very homogeneous. Finally the higher the percentage of combined maleic anhydride in the rubber, the more difficult it is to dissolve the product.

One faces, then, the dilemma of whether to start with rubber containing a relatively high percentage of combined maleic anhydride and obtain a product which is difficultly soluble and gives only mediocre bonds on metal or, as an alternative, to start with rubber containing relatively little combined maleic anhydride, *i.e.*, 15 per cent as a maximum, and obtain a soluble product which gives good bonds, but the thermoplasticity of which is reduced relatively little.

Knowledge now available on the reaction between rubber and maleic anhydride makes possible an understanding of these phenomena. Actually maleic anhydride becomes fixed on the rubber<sup>6</sup>, and in this way restricts the



possibility of subsequent reaction with phenolsulfonic acid by forming, through the setting up of intermolecular bridges, a product which is more or less vulcanized and the solubility of which depends on the degree of vulcanization.

To reduce the thermoplasticity without reducing either the solubility or the adhesive properties, it is necessary for a second reaction to take place after the reaction with phenolsulfonic acid and after applying the resulting product, *i.e.*, the desired modification in the Thermoprene should take place at the moment of vulcanization.

#### APPLICATION OF THE PROSTHESIS-SYNESIS REACTION TO RUBBER MODIFIED BY PHENOLSULFONIC ACID

Dufraisse and Compagnon<sup>7</sup> have shown that the condensation of formaldehyde with phenols can bring about the vulcanization of rubber. The principle of the reaction, to which has been given the name of prosthesis-synthesis, involves two steps: (1) addition of a phenol to the rubber hydrocarbon (prosthesis); (2) union, by means of formaldehyde, of the rubber chains carrying the phenol molecules (synesis).

The first step in this process is closely analogous to the treatment which Fisher applied to rubber. In the case of prosthesis, the reaction is with a phenol (resorcinol); in the other case the reaction is with phenolsulfonic acid. Although it may have been assumed that phenolsulfonic acid brings about a cyclization or isomerization of the rubber, it may be asked whether, in reality, there may not actually be simple and direct fixation of the phenolsulfonic acid on the rubber hydrocarbon and whether, accordingly, by a synesis reaction, a kind of vulcanization takes place, the effect of which would be to reduce the thermoplasticity. This hypothesis led the present authors to study the action of formaldehyde and to determine whether by its action it would be possible to unite the molecules of rubber previously modified by fixation of phenolsulfonic acid.

The attempt was first made to incorporate trioxymethylene in commercial Phenolac<sup>8</sup>. The process is not easy, for if a mixing mill is used for this purpose, it must be heated to about 70° C, a temperature below which the plasticity of the product is not great enough for the mass to be passed through the rolls. But at 70° C and as a result of the milling, trioxymethylene is transformed into formaldehyde, which is evolved immediately. This phenomenon made it possible in addition to prove that there is a very definite effect on the structure of the product. In reality, although after incorporation of 1 per cent of trioxymethylene, the Phenolac is still soluble in ordinary solvents of rubber, after incorporation of more than 2 per cent, the product swells but does not dissolve. This is proof that there is some sort of reaction, and it indicates that advantage may be taken of it in the problem at hand.

It should be mentioned once more that, although the chief aim was to render Thermoprene less thermoplastic, it was, nevertheless, necessary for it to retain sufficient solubility to be used in the form of a solution, particularly when the rubber was to be bonded to metal. Hence for the condensation reaction to be applicable, it must not take place until the moment of vulcanization of the rubber. With this in view, one of the first attempts was to add trioxymethylene in some other way than on a mill. It might have been convenient for example, to use two solutions, one containing only trioxymethylene, and to mix them at the moment when the operation was to be carried out. However, trioxymethylene is not soluble in ordinary solvents of rubber. The attempt was therefore

made to replace trioxymethylene by other compounds. These experiments were carried out in the following way. A solution of Thermoprene containing the compound being tested was heated in a sealed tube. For the compound to be of any promise, it was essential for it to bring about gelation of the solution after heating, whereas at ordinary temperature it was just as necessary for the solution to remain completely liquid. Among the various compounds which were tested, the one which fulfilled these conditions best was hexamethylenetetramine. The technique of heating in a sealed tube made it possible to determine the percentage of hexamethylenetetramine required to bring about the most nearly complete and most rapid gelation. This was found to be of the order of 8 per cent.

#### A TENTATIVE INTERPRETATION OF THE ACTION OF HEXAMETHYLENETETRAMINE ON THERMOPRENE

If the mechanism of prosthesis-synthesis proposed by Dufraisse and Compagnon<sup>7</sup> is accepted, then it must be assumed that phenolsulfonic acid combines, at least in part, with the rubber hydrocarbon. Among the hypotheses which can be advanced to explain this combination, the ones which are worthy of consideration are first of all those which involve the fixation of phenolsulfonic acid on the double bond. The role of hexamethylenetetramine would then be to unite by methylenic groups the phenolic nuclei thus combined with the rubber hydrocarbon. The formation of a three-dimensional network decreases the thermoplasticity by having the same effect as vulcanization.

This view is in good accord with two experimentally established facts; first, the impossibility of extracting phenolsulfonic acid from modified rubber, and secondly, the decrease in thermoplasticity brought about by agents capable of condensation with phenolsulfonic acid.

#### EXPERIMENTAL DETAILS

The reaction of phenolsulfonic acid with rubber modified by maleic anhydride did not give sufficiently interesting results to make it seem advisable to reconsider them. On the contrary, the effects of hexamethylenetetramine on commercial Phenolac were studied in detail, and certain observations now merit recording.

*Influence of the proportion of hexamethylenetetramine and of the temperature of treatment.*—In this study a 40 per cent solution of Phenolac in carbon tetrachloride was heated in sealed tubes under various conditions and with increasing proportions of hexamethylenetetramine. The choice of carbon tetrachloride was justified as a safety measure; its noninflammability made it possible to seal the tubes without danger. The tubes, two-thirds full and sealed, were placed in a resistant metal tube, in which they were then heated by placing the metal tube in an oven at the desired temperature and for the desired time. In this way it was proved that the temperature necessary for the reaction to take place is above 150° C, whatever the proportion of hexamethylenetetramine, and even when the heating is prolonged far more than one hour. It is inadvisable to use higher temperatures, for this leads to difficulties in vulcanizing.

The proportion of hexamethylenetetramine to be used is close to 8 per cent. With less than this percentage, gelation does not take place readily; above this percentage, there does not seem to be any increase in the firmness of the gel.

The precision of this method of experimentation is not very great, and the results obtained are, in general, only qualitative. Attempts were made to obtain more exact data by measuring the plasticity and the hardness at different temperatures, but this could not be done with the apparatus available at the

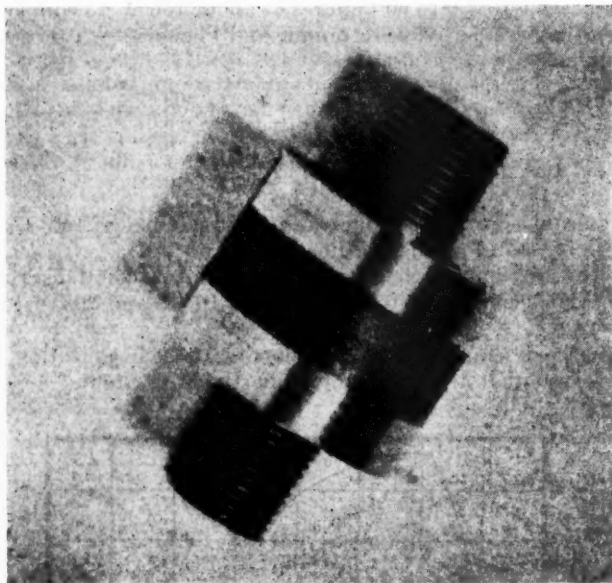


FIG. 1.—Rubber-to-metal test-specimen for measuring bond separation.

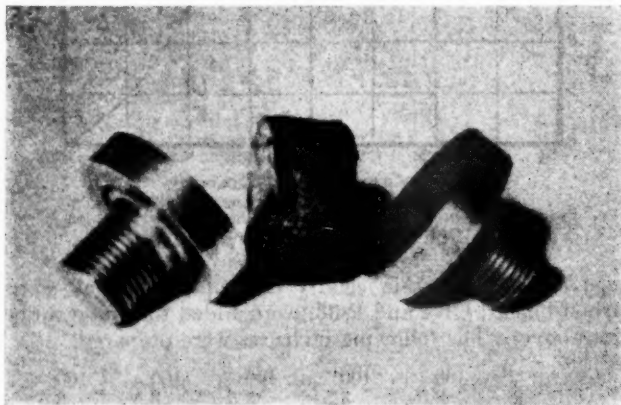


FIG. 2.—Three parts of the test-specimen before assembly. The coating of adhesive is visible on the right-hand sectional part.

time. Accordingly it was decided to prepare rubber-to-metal test-specimens by the standard method of the American Society for Testing Materials (see Figures 1 and 2), and measure the load necessary to separate the bond at different temperatures.

The next question was the choice of rubber stock to be bonded to the metal. Hexamethylenetetramine is a relatively weak accelerator; nevertheless, because of its basic character, it is capable of activating to a considerable extent acidic accelerators. It was necessary, therefore, to avoid rubber mixtures containing acid accelerators, inasmuch as preliminary experiments showed the necessity of heating for 30 to 60 minutes at about 150° C to complete the reaction between the hexamethylenetetramine and Phenolac. After various trials, the following mixture was chosen:

Rubber	100
Sulfur	3.5
Di- <i>o</i> -tolylguanidine	0.3
Triphenylguanidine	1
Zinc oxide	10

which was vulcanized to its optimum state in 35 minutes at 152° C. This cure was adequate for transforming the Phenolac.

This rubber mixture was then bonded between two metal discs by means of Phenolac solutions containing 6, 8, 10, 12, 14, 16, 18 and 20 per cent of hexamethylenetetramine.

A curve of the dynamometric measurements, after vulcanization, of the bond at 100° C showed that the optimum proportion was around 8 per cent (see Figure 3).

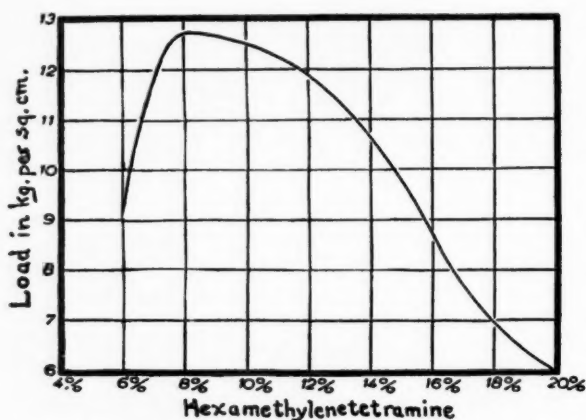


Fig. 3.—Influence of the content of hexamethylenetetramine on the force required for separation.

*Influence of loading.*—Certain clearly defined phenomena were observed when two carbon blacks, CK4 and P-33, were added to a base rubber mixture similar to that above. The following mixtures were prepared.

Rubber	100	100	100	100	100	100
Sulfur	3.5	3.5	3.5	3.5	3.5	3.5
Di- <i>o</i> -tolylguanidine	0.3	0.3	0.3	0.3	0.3	0.3
Triphenylguanidine	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5
P-33 black	15	12	9	6	3	0
CK4 black	0	3	6	9	12	15

It was found that, at least in the proportions used, P-33 black had no effect on the strength of bond, whereas CK4 black reduced considerably the strength

of the bond when present in amounts greater than 3 per cent by weight of the rubber. The pH values of these blacks are practically identical (neutral or acid), and they differ most in their absorptive or reënforcing power.

On the contrary, two other fillers having almost the same absorptive or reënforcing power, *viz.*, magnesium carbonate and kaolin, showed effects very different from those of the two carbon blacks. Magnesium carbonate imparted very poor adhesion, whereas with kaolin the adhesion was quite satisfactory. The pH values of these two fillers are very different; in fact kaolin is acidic, whereas magnesium carbonate is highly alkaline.

Finally it should be added that the filler which gave the best bonds was whiting having a pH value above 7 but lower than that of magnesium carbonate.

The influence of fillers on the adhesion does not, therefore, depend on their pH values nor on their reënforcing power. Unfortunately the experiments described in the present paper do not give any clue as to what factor is involved.

#### REFERENCES

- <sup>1</sup> See "Handbuch der Gesamten Kautschuktechnologie", edited by Hauser, Union Deutsche Verlagsgesellschaft, Berlin, 1935, p. 1581.
- <sup>2</sup> Harries, *Ber.* **56**, 1050 (1923).
- <sup>3</sup> Fisher, *Ind. Eng. Chem.* **19**, 1325 (1927).
- <sup>4</sup> Compagnon and Le Bras, *Compt. rend.* **212**, 616 (1941); *Rev. gén. caoutchouc* **18**, 89 (1941); Compagnon and Bonnet, *Rev. gén. caoutchouc* **19**, 79 (1942).
- <sup>5</sup> A chlorinated wax marketed by Pechiney.
- <sup>6</sup> Le Bras, *Rev. gén. caoutchouc* **19**, 43 (1942).
- <sup>7</sup> Dufraisse and Compagnon, *Rev. gén. caoutchouc* **18**, 40 (1941).
- <sup>8</sup> This Phenolac was kindly furnished by the Société Colombes-Goodrich.

# DETERMINATION OF RESISTANCE TO ABRASIVE WEAR.

## V. INFLUENCE OF CALENDER GRAIN \*

R. W. PARRIS AND J. R. SCOTT

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

The standard form of test-piece used on the type of abrasion testing machine<sup>1</sup> of the Akron Standard Mold Company is a disc of about 63.5 mm. diameter and 12.5 mm. thick. This can be made either (1) by vulcanizing in a mold of appropriate shape, which is filled with a blank cut from a sheet of stock about 13 mm. thick, or (2) by cutting out from a mold-vulcanized slab 12.5 mm. thick. In either case the abrasive wear takes place on a surface corresponding to the edge of a disc cut from the sheet of stock. The same is true if tests are made on discs cut from rubber articles such as soles, flooring, or other material in sheet form.

In the actual use of such articles as tires, soles and heels flooring, conveyor belting, and tough rubber cable sheaths, the abrasive wear occurs on a surface representing substantially the flat surface of the sheet of stock. If the stock contains fillers that produce a calender grain effect, *e.g.*, magnesium carbonate and clay, it cannot be assumed that the wear on the flat surface of the sheet is the same as that on the edge of a disc cut from it, which lies in a plane perpendicular to the former surface. If there is a difference between the rates of wear on these two surfaces, the type of test-piece described above must give an incorrect indication of the abrasion resistance of the rubber in actual use.

As there appeared to be no published information on the effect of calender grain on abrasion resistance, experiments were made to see whether such an effect existed. For this purpose the following mixings, of the brown shoe-soleing type, were used:

	A	B	C	D
Smoked sheet	100	100	100	100
Sulfur	3.5	3.5	3.5	3.5
Stearic acid	2	2	2	2
Mineral rubber	8	8	8	8
Zinc oxide	10	10	10	10
Iron oxide	12	12	12	12
Di-o-tolylguanidine	0.5	0.5	0.5	0.5
Mercaptobenzothiazole	0.5	0.5	0.5	0.5
Silica	135	—	—	—
Magnesium carbonate	—	135	—	—
China clay (high grade)	—	—	200	—
China clay (low grade)	—	—	—	200

The silica was an amorphous variety which was expected to produce no grain effect.

\* Reprinted from the *Journal of Rubber Research*, Vol. 16, No. 5, pages 127-128, May 1947. Part IV is published in the *Journal of Rubber Research*, Vol. 16, No. 5, pages 125-127, May 1947.



Abrasion specimens of approximately the standard dimensions were prepared by two methods:

(1) The stock was sheeted out on an even-speed mill to about 13 mm. thickness and vulcanized in a mold to give a slab 12.5 mm. thick; from this discs of 63 mm. diameter were cut.

(2) A disc of 53 mm. diameter was cut from a sheet of stock 13 mm. thick, and round the edge of this core was wrapped a strip 13 mm. wide of stock sheeted out about 5 mm. thick; the whole was then vulcanized in a special mold, giving a disc 63 mm. diameter and 12.5 mm. thick.

The times of vulcanization, representing in each case three-fourths of the time giving optimum tensile properties, were as follows: A, 34; B, 38; C, 68; D, 30 min. at 130° C.

A 7-minute rise at vulcanizing temperature was given before applying hydraulic pressure to the ram of the press.

The specimens were tested under standard conditions already laid down<sup>1</sup>, weighings being made after every 500 revolutions and the average abrasion losses between 1000 and 2500 revolutions used to calculate the result.

It will be evident that with specimens of type (1) the test is made on a surface corresponding to the edge of the sheet of stock (edge test), whereas with type (2) the test is made on the flat surface of the sheet (flat test).

To make certain that the use of different types of molds for specimens (1) and (2) did not result in a difference in degree of vulcanization, the (2) specimens, after being tested in the ordinary way, were buffed down to 52 mm. diameter so as to expose the core, and then tested again, using a supporting washer of 44 mm. diameter so as to give the standard projection of 4 mm. beyond the edge of the washer. It will be obvious that this second test represents an edge test. As it was thought that the alteration in diameter might affect the abrasion loss, the (1) specimen of Mixing C was similarly buffed down and tested for comparison with the buffed-down (2) specimen.

The results of the abrasion tests, all of which were made between 19° and 23° C, are given in Table 1.

TABLE 1

Mixing	Specimen (1)		Specimen (2)	
	Original (edge test)	Buffed down (edge test)	Original (flat test)	Buffed down (edge test)
A	0.63	—	{0.64 0.645	{0.59 0.57
B	0.275	—	0.68	0.27
C	0.39	0.36	{0.80 0.785	{0.33 0.37
D	0.645	—	1.215	0.84

Abrasion loss is expressed in cc. per 1000 revolutions of the abrasive wheel. Where duplicate tests were made, the separate results are given.

The main conclusions indicated by these results are:

(1) Both types of test-piece, when buffed down to 52 mm. diameter so as to give edge tests, give substantially the same results (Mixing C). This shows that the use of the different types of mold has not introduced any marked variation.

(2) Reducing the diameter of Type (1) from 63 mm. to 52 mm., which does not alter the character of the test, lessens the abrasion loss by about 8 per cent (Mixing C). With Mixings A and B the difference between Type (1), original diameter, and Type (2), buffed down, is likewise attributable simply to the difference in diameter, but the results for Mixing D are anomalous in that the difference is reversed.

(3) Reducing the diameter of Type (2) from 63 mm. to 52 mm., *i.e.*, changing from a flat to an edge test, reduced the abrasion loss by the following amount: A, 9%; B, 60%; C, 56%; D, 30%. The reduction with Mixing A can be accounted for by the change in diameter (*cf.* paragraph (2) above); this indicates the absence of any noticeable grain effect, as was expected. With Mixings B, C, and D, however, there is a pronounced grain effect, the ratio of abrasion losses in the flat and edge tests being as high as 2.5 to 1 with the magnesium carbonate mixing.

The results of these tests indicate, therefore, that with rubbers containing anisotropic fillers, which produce a grain effect, abrasion on the Akron machine may be much more rapid on a flat surface (parallel to the plane of the calendered sheet of stock) than on an edge surface (perpendicular to this plane).

As rubber is generally used so that wear occurs on a flat surface, it is suggested that tests should normally be made on specimens that present such a surface to the abrasive wheel, instead of an edge surface, as in the present type of specimen.

If the results obtained with the Akron machine can be taken as representing what happens in service wear, it would appear that rubbers containing anisotropic fillers, when used so that wear occurs on a flat surface, are not giving the best results of which they are capable.

In this connection reference may be made to a patent<sup>2</sup> for making solid tires by cutting extruded stock lengthwise to form two tires having the cut surfaces as the treads. It is claimed that in the ordinary solid tire, where the outside of the extruded mass forms the tread, the grain is parallel to the tread, so cuts, once started, extend along the grain by tearing, thus causing rapid destruction of the tire, whereas in the patented type of tire this is avoided, because the grain, which runs round the extruded mass helically, is substantially perpendicular to the tread surface.

If grain effects can produce such large differences in abrasion resistance as are indicated by the present experiments, the amount of grain (degree of anisotropy of the stock), which depends on the method of milling and(or) calendering, must have quite a marked influence on the abrasion resistance of any given type of surface, *i.e.*, flat or edge.

#### REFERENCES

- <sup>1</sup> Daynes, J. *Rubber Research* 9, 15 (1940). This is Part I of the present series on the "Determination of Resistance to Abrasive Wear" and deals with "Tests on the Akron Standard Mold Company's type of machine".
- <sup>2</sup> Dunlop Rubber Co., Ltd., British patent 242,246; *India-Rubber J.* 71, 232 (1926).

# VII. UNIFORMITY OF RESULTS OBTAINED WITH THE DU PONT MACHINE \*

J. F. MORLEY AND J. R. SCOTT

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

The du Pont or Grasselli abrasion testing machine uses emery paper as the abrasive, and as a fresh piece of paper is normally used for each rubber tested, it is important to know whether any appreciable variability in test results arises from nonuniformity of the paper. It is desirable to know also whether the rate of abrasion varies during any one test and whether any variation in the abrasive qualities of the paper occurs during the three test runs that are normally made with the same rubber on the one piece of paper. In the present work the abrasive used was that recommended by the American Society for Testing Materials<sup>1</sup>.

Five hundred sheets of this emery paper were purchased as a stock for use with the machine, and from this lot the sheets for the following tests were taken.

As the mold used for vulcanizing the 2-cm. square test-specimens was the standard 6-cavity mold<sup>2</sup>, and only one mold was available, the number of sheets of emery paper tested was limited to 6. Six lots of specimens were vulcanized, making 36 in all. Each set of 6 specimens required for the normal triplicate test was made up by taking one specimen from each lot of 6 vulcanized together. By this means the effects of any inequalities in the vulcanizing conditions were minimized, and it was possible to carry out tests on 6 sheets of emery paper. The sheets chosen were numbers 80, 160, 240, 320, 400, and 480, counting from the top of the pile.

The following mixing was used: washed smoked sheet 100, sulfur 3.1, MPC black 38.2, zinc oxide 7.6, stearic acid 3.1, mercaptobenzothiazole 0.76.

This mixing, when vulcanized as sheets 0.1 inch thick in a platen press at 148° C, gave the following tensile results, using dumb-bells with 1 in.  $\times$   $\frac{1}{4}$  in. test-length.

	Vulcanization	
	30 min.	40 min.
Tensile strength (lb. per sq. in.)	4000	4060
Elongation at break (%)	595	575
Modulus (lb. per sq. in.) at 100% elongation	300	330
Modulus (lb. per sq. in.) at 300% elongation	1310	1450
Modulus (lb. per sq. in.) at 500% elongation	3105	3340

The abrasion specimens were vulcanized for 35 min. at 148° C, and were then kept for about a week before the tests were made. These vulcanizates had a specific gravity of 1.119 at 15°/15° C.

The abrasion machine used conformed to the requirements of the A.S.T.M., the test conditions being as follows:

Total load pressing specimens against abrasive	8 lbs.
Speed of revolution of abrasive	37 r.p.m.
Mean linear speed of abrasive	48 ft. per min.
Air pressure used for blast to clean abrasive	25 lbs. per sq. in.
Temperature of test	70°-77° F

\* Reprinted from the *Journal of Rubber Research*, Vol. 16, No. 5, pages 130-134, May 1947. Part VI is published in the *Journal of Rubber Research*, Vol. 16, No. 5, pages 129-130, May 1947.

With each paper 3 tests, each using a pair of specimens, were made. Each pair of specimens was given a preliminary run until the two specimens appeared to be seating evenly; this run was not reckoned as part of the test. The actual test-run lasted 20 minutes, the specimens being weighed before the run and

TABLE 1  
ABRASION LOSS (GRAMS)

Emery paper No.	L.H. test-piece		R.H. test-piece	
	10-min. run	20-min. run	10-min. run	20-min. run
80	0.344		0.393	
	0.336	0.680	0.360	0.753
	0.300		0.324	
	0.327	0.627	0.312	0.636
	0.338		0.355	
	0.383	0.721	0.391	0.746
160	0.389		0.406	
	0.382	0.771	0.362	0.768
	0.402		0.397	
	0.377	0.779	0.387	0.784
	0.392		0.428	
	0.367	0.759	0.398	0.826
240	0.355		0.391	
	0.402	0.757	0.394	0.785
	0.355		0.370	
	0.342	0.697	0.382	0.752
	0.363		0.404	
	0.361	0.724	0.374	0.778
320	0.383		0.361	
	0.376	0.759	0.377	0.738
	0.402		0.403	
	0.411	0.813	0.418	0.821
	0.395		0.423	
	0.381	0.776	0.391	0.814
400	0.363		0.387	
	0.384	0.747	0.366	0.753
	0.423		0.394	
	0.396	0.819	0.366	0.760
	0.353		0.360	
	0.351	0.704	0.350	0.710
480	0.396		0.407	
	0.409	0.805	0.396	0.803
	0.384		0.342	
	0.351	0.735	0.340	0.682
	0.367		0.361	
	0.367	0.734	0.378	0.739

again after periods of 10 and 20 minutes. The weighing after 10 minutes was included to determine whether the rate of abrasion varied during the 20-minute period.

Readings of the spring balance, attached to the arm holding the specimens, were taken every 2 minutes during the test-run. From the average of these readings and the constants of the machine, the energy consumed in abrading the specimens was determined, thus enabling the abrasion loss to be expressed: (1) as a volume loss (cc.) per hour; (2) as a volume loss (cc.) per horse-power-hour.

As the arm which carries the specimens was not free to oscillate in a plane perpendicular to that of the abrasive, it could not be assumed that the 8-lb. load is equally divided between the two specimens. As a check on the equality or otherwise of the pressures, the results for each individual specimen are recorded in Table 1. The upper figure of each pair is the loss during the first 10 minutes, and the lower figure that during the second 10 minutes. Results are given for three tests, with different specimens, on each paper, the top results relating to the first test and the bottom results to the last test. The terms L.H. and R.H. refer to the left and right specimens as seen when facing the machine.

The data in Table 1 can best be studied by means of the statistical method of analysis of variance, the results of which are given in Table 2. The difference

TABLE 2  
ANALYSIS OF VARIANCE

	Source of variation	Sums of squares	Degrees of freedom	Variance	Variance ratio	
a	Between sides	0.00081	1	0.00081	—	0.92
b	Between papers	0.01604	5	0.00321	—	3.7
c	Interaction S $\times$ P	0.00293	5	0.00058	—	0.66
d	"Samples plus runs"	0.02104	24	0.00088	3.4	1.0
e	Error	0.00951	36	0.00026	1.0	—
	Total	0.05033	71			

between any two 10-minute runs on one pair of specimens can be used as a measure of the reproducibility of the test when performed under nearly identical conditions (the paper may wear slightly between the runs, but this effect has been neglected) and there are 36 independent comparisons of this kind (three on each paper for each side of the machine), thus giving 36 degrees of freedom for error in line (e) of Table 2. The variation between the 20-minute runs will be greater than the error variation because different pairs of specimens were used for these comparisons and, in addition, any loss of abrasiveness of the paper influences these results more than the 10-minute values. There are 24 independent comparisons of this nature (two on each paper for each side of the machine), and the corresponding 24 degrees of freedom are referred to in Table 2 as "samples plus runs variation," in line (d) of Table 2. The remaining eleven degrees of freedom out of the total of 71, represent the one d.f. between the two sides of the machine, the 5 d.f. between the six paper discs, and the 5 d.f. for interaction between papers and sides. The conclusions to be drawn from the analysis of variance are:

1. The error of a single test figure (one 10-min. run) is reasonably small and has a standard deviation of  $\pm 0.016$  gram, or about 4.5 per cent of the mean test figure.

2. It is not possible in this experiment to separate the sample variation from that due to the wear on the paper, but the combined effect is considerable, as is shown by the highly significant variance in line (d) of Table 2, and this new figure must therefore form the practical basis for assessing the error, in place of the now somewhat artificial figure in line (e).

3. The differences between the 6 sheets of abrasive paper are significant, even in comparison with the combined variation for samples and runs, as is shown by line (b) of Table 2, and it is thus clear that paper-variation may be a serious limiting factor in abrasion-testing. It should be pointed out that this is not always the case, and other unpublished experiments at the R.A.B.R.M. have at times shown no significant variation between the papers; the experiments should, however, always be designed in such a way that paper-variation can be eliminated if necessary.

4. The difference between the two sides of the machine was not significant in this experiment (see line (a) of Table 2), but a warning should be given that this is by no means a universal feature of du Pont abrasion tests or machines, other unpublished work from the R.A.B.R.M. and other laboratories having revealed serious differences between the left- and right-hand sides. Here, again, good experimental design enables the variation to be eliminated, should this course prove desirable.

5. The interaction between sides and papers is not significant (see line (c) of Table 2); this indicates that the differences which were found between the sheets of paper effect equally results from both sides of the machine, no differential effect being present.

The abrasion losses expressed as cc. per hour (or horse-power-hour), calculated from the sum of the 20-minute readings for left and right specimens, are given in Table 3, the three sets of results quoted for each emery paper corresponding to the three tests with different pairs of specimens.

No satisfactory conclusions can be drawn about any change in abrasiveness of the papers during the three test-runs, since it is not known how the samples from the different molds were distributed among the runs on the papers. Other, as yet unpublished, experiments at the R.A.B.R.M. have shown definite loss of abrasiveness of the papers as they are used, a conclusion which differs from that of Okita<sup>3</sup>, that one sheet of emery can be used 5 times.

It is interesting to compare these results with those of Klamann<sup>4</sup>. In a series of 18 tests made on one day he found maximum deviations from the mean of +12 per cent and -15 per cent, the average deviation being 8 per cent. In a series of 10 tests on successive days the corresponding figures were +6, -7, and 2.8 per cent. The details given by Klamann are unfortunately insufficient to indicate the contributory causes of these divergencies.

## CONCLUSIONS

(1) Tests have been made to investigate the variability of the abrasive papers used on the du Pont abrasion machine; the data obtained have also been examined to detect any variation in rate of abrasion during one test, and differences between the right- and left-hand specimens.

(2) Differences in abrasiveness of 13 per cent were found between the different sheets of emery paper, even when compared with the differences between the rubber specimens, and it is considered that a solid disc of bonded abrasive, as used on the Akron machine, would be preferable to emery papers.



TABLE 3

Emery paper No.	Volume loss (cc. per hr.)	Energy consumed (H.P.)	Volume loss (cc. per H.P. hour)
80	3.84	0.0202	189
	3.38	0.0197	172
	3.93	0.0198	199
Mean	3.72	0.0199	187
160	4.12	0.0203	203
	4.19	0.0209	201
	4.25	0.0206	206
Mean	4.19	0.0206	203
204	4.14	0.0202	205
	3.87	0.0207	187
	4.03	0.0206	195
Mean	4.01	0.0205	196
302	4.02	0.0206	195
	4.38	0.0204	214
	4.25	0.0207	206
Mean	4.23	0.0206	205
400	4.04	0.0201	199
	4.23	0.0207	202
	3.78	0.0209	173
Mean	4.01	0.0206	195
480	4.31	0.0208	207
	3.81	0.0207	184
	4.21	0.0204	206
Mean	4.11	0.0206	199

(3) As there is no evidence of variation in rate of abrasion during a 20-minute run, there seems to be no objection to using different test-periods for different rubbers if circumstances render this desirable.

(4) There are small, but not consistent, differences between the abrasion losses on the right- and left-hand specimens, which may arise from the 8-lb. load not being equally distributed between them. It is considered that the machine could be improved by making the arm that carries the specimens free to oscillate in a plane perpendicular to the abrasive, so that the loads on the specimens would be automatically equalized. The practice of rigidly fixing the arm parallel to the plane of the abrasive seems unsound because, if the parallelism were really rigid, the rates of wear on the two specimens would of necessity be equal, even if the rubbers had different abrasion resistances. Moreover, any suggestion to test the sample under examination and a standard rubber simultaneously is clearly unsound unless a freely oscillating arm is provided.

#### REFERENCES

- <sup>1</sup> No. 0 Emery paper, supplied by the H. L. Scott Co. See Am. Soc. Testing Materials, Standards on Rubber Products, D394-40.
- <sup>2</sup> Am. Soc. Testing Materials, Standards on Rubber Products, D394-40.
- <sup>3</sup> Okita, *J. Soc. Chem. Ind. Japan* **38**, Suppl. binding 534 (1935); *RUBBER CHEM. TECH.* **9**, 502 (1936).
- <sup>4</sup> Klamann, *Proc. Am. Soc. Testing Materials* **31**, II, 936 (1931).

# HARDNESS TESTING OF VULCANIZED RUBBER.

## V. INVESTIGATION OF THE BALL INDENTATION TEST. PART 3. CONDITION OF THE RUBBER SURFACE \*

E. H. DOCK AND J. R. SCOTT

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS, CROYDON, ENGLAND

### INTRODUCTION

The surfaces of rubbers on which hardness tests are made may vary considerably. They may be smooth or rough, *e.g.*, clothmarked, clean or coated with French chalk, paraffin wax, or other bloom. It is, therefore, important to know how these differences affect the readings obtained with the indentation type of hardness tester.

It is obvious that the roughening of the surface produced by clothmarking must affect the results of an indentation test. Consideration of the mechanism of the test shows, moreover, that any factor which alters the coefficient of friction between the rubber and the indenting ball or the rigid supporting surface must affect the hardness reading. When an indentation is produced in the rubber, the upper surface is stretched and must, therefore, tend to slip over the surface of the ball. Again, the rubber between the ball and the supporting surface is compressed and must, therefore, expand laterally. Both top and bottom surfaces thus tend to slip over the surfaces in contact with them, and the more easily the slippage occurs, the more readily does the rubber give way to the indenting ball. Hence, the less the friction between the rubber and the ball and(or) supporting surface, the higher is the reading. The nature of the rubber surface would, therefore, be expected to have some effect, though not necessarily an important one, on the results.

The experiments described below were made with the object of finding the magnitude of the effects produced by various modifications in the nature of the surface.

### EXPERIMENTAL

Except where otherwise stated, the tests were made with the R.A.B.R.M. hardness gauge, using a 1-kg. load allowed to act for 1 minute (no zero load was used), with the rubber supported on a glass plate. The *hardness number* is the depth of indentation in mm./100, and each value quoted is the mean of four readings.

#### TESTS ON RUBBERS OF NORMAL THICKNESS

By normal thickness is meant the thickness normally used for hardness tests (5 to 10 mm.).

\* Reprinted from the *Journal of Rubber Research*, Vol. 16, No. 9, pages 134-141, May 1947. Part 2 was published in the *Journal of Rubber Research*, Vol. 13, No. 1, pages 19-22, January 1944.

*Effects of French chalk, castor oil, and roughening of the surface*

Tests were made on a miscellaneous collection of rubbers, ranging from the hardest to the softest normally met with. They were all free from paraffin-wax bloom. French chalk was examined because it is often present on rubber goods. Castor oil was included to show, in an exaggerated degree, the effect of altering the coefficient of friction between the rubber ball and supporting surface, since it is an excellent lubricant with no swelling action on rubber. Results are given in Table 1.

TABLE 1  
HARDNESS NUMBER ( $\frac{1}{4}$ -INCH BALL)

- (1) Untreated.
- (2) French chalk applied liberally to top surface.
- (3) As (2) with excess chalk wiped off.
- (4) Top surface lubricated with castor oil.
- (5) Top surface roughened with emery paper.
- (6) French chalk applied as in (3) to bottom surface.
- (7) Bottom surface lubricated with castor oil.

Rubber	Thick- ness (mm.)	1	2	3	4	5	6	7
A	5	17.0	—	18.5	17.0	18.5	—	—
B	5	18.5	19.0	19.0	18.0	20.5	18.5	20
C	5	29.5	33.5	30.5	32.5	32.5	—	—
D	9	43	—	—	43	—	—	—
E	9.5	53	55	56	56	56.5	53.5	56
F	9.5	64	65.5	68	67	66.5	—	—
G	9	87	—	—	87	—	—	—
H	9.5	90.5	90	93	94	92	—	—
J	9	109	—	—	115.5	—	—	—
K	9	115	—	—	121	—	—	—
L	9	127.5	—	—	128	—	—	—
M	9.5	135.5	136.5	139.5	145.5	138.5	—	—
N	9.5	149.5	148.5	155	156	152	149	150.5
P	9	151.5	—	—	168	—	—	—
Q	9	170	169.5	177.5	183.5	170	173.5	181.5

French chalk never produces more than a small effect, which is almost always an increase. There are indications that it has more effect when applied in small amounts or when applied to the bottom instead of the top. Although individual results are irregular, the effect of French chalk tends to be greater on the softer rubbers, as might be expected (see Table 2), though it

TABLE 2  
INCREASE IN HARDNESS NUMBER DUE TO LUBRICATION  
WITH FRENCH CHALK

Rubber	Top surface (mean of tests (2 and 3))	Bottom surface (test 6)	Mean of group
A } hard	1.5	—	1.1(5%)
B } hard	0.5	0.0	
C } hard	2.5	—	
E } medium	2.5	0.5	1.7(2.5%)
F } medium	2.8	—	
H } medium	1.0	—	
M } soft	2.5	—	2.1(1.4%)
N } soft	2.5	-0.5	
Q } soft	3.5	3.5	

does not increase proportionately with the hardness number, as the percentage figures in brackets show (these are given as percentage of the mean hardness number).

Castor oil has a greater effect than French chalk, at least on the softer rubbers, as would be expected from its better lubricating power, and here the increase is more nearly proportional to the hardness number (see Table 3).

TABLE 3  
INCREASE IN HARDNESS NUMBER DUE TO LUBRICATION WITH CASTOR OIL

Rubber	Top surface (Test 4)	Bottom surface (Test 7)	Mean of group
A	0.0	—	0.8(3%)
B	-0.5	1.5	
C	3.0	—	
D	0.0	—	
E	3.0	3.0	2.5(3.5%)
F	3.0	—	
G	0.0	—	
H	3.5	—	
J	6.5	—	4(3.5%)
K	6.0	—	
L	0.5	—	
M	10.0	—	10(6.5%)
N	6.0	1.0	
P	16.5	—	
Q	13.5	11.5	

Roughening the surface increases the reading slightly, the increase being apparently independent of the hardness (see Table 4).

TABLE 4  
INCREASE IN HARDNESS NUMBER DUE TO ROUGHENING

Rubber	Increase
A	1.5
B	2.0
C	3.0
E	3.5
F	2.5
H	1.5
M	3.0
N	2.5
Q	0.0
Mean	2.2

It seems unlikely that this increase can be due to a change in the coefficient of friction between rubber and ball, since this would presumably be increased by roughening and the indentation thereby decreased. The observed increase is more probably due to the fact that the rough uneven surface is flattened down by the ball, owing to the high pressure per unit area, but not by the foot of the gauge, which exerts a much smaller pressure, so that the indentation reading is increased by the extent of the flattening (*cf.* effect of clothmarking, below).

The influence of the various treatments on the consistency of repeat readings (at different points on the sample) was examined by taking the range,

i.e., the difference between the highest and lowest, of each set of four readings. The results for rubbers A, B, C, E, F, H, M, N, and Q are summarized in Table 5; treatments 6 and 7 are not included because only a few rubbers were tested.

TABLE 5  
RANGE OF FOUR READINGS

Treatment	1	2	3	4	5
Smallest difference	2.0	1.0	1.0	1.5	2.0
Largest difference	5.5	3.5	7.5	6.0	6.5
Mean difference	4.4	2.4	4.5	3.4	3.6

None of the treatments, except possibly liberal dusting with French chalk (No. 2), has any marked influence in improving the consistency.

#### *Effect of paraffin wax bloom*

Several rubbers were selected that contained paraffin wax and had been stored long enough to develop a pronounced waxy bloom. These were tested first without treatment and again after rubbing off the wax with a cloth moistened with methylated spirit (it was not thought advisable to use a hydrocarbon liquid, which would have been a better solvent, owing to its ready absorption by the rubber). The results are shown in Table 6, the last two columns giving the range.

TABLE 6

Rubber	Thickness (mm.)	Hardness number (1/4-inch ball)		Range	
		Untreated	Cleaned	Untreated	Cleaned
R	5.1	19.0	19.0	2.0	1.0
S	9.5	22.5	23.5	2.0	4.0
T	9.5	101	105	3.5	4.0
U	9.5	110	111	2.0	4.0
V	9.5	122.5	124	6.0	6.0
W	9.5	135.5	136.5	3.0	3.0
			Mean	3.1	3.7

Contrary to expectation, the cleaned surface usually gives a bigger hardness number than the waxy surface; however, this effect of cleaning appears to be real, by comparison with the error of measurement. Cleaning has little effect on the consistency of the readings.

#### *Effect of clothmarking*

*Series A.*—Experiments were made first on the back surfaces of rubber floorings which were clothmarked by fabrics of varying degrees of coarseness. Tests were made on samples treated as follows: (1) untreated; (2) after buffing off the clothmarking on a fine abrasive wheel and then allowing to rest for a few hours; (3) repeat test on (2) 11 days later.

As it was difficult to make the buffed surface perfectly flat, the Pusey-Jones Plastometer was used instead of the R.A.B.R.M. gauge, since the latter may give incorrect results if the test-piece is not flat. The results are given in Table 7.

The first effect of buffing, test (b), was to increase the hardness number slightly on all except the most coarsely marked sample, No. 1. The later tests (c), however, showed in all cases a small decrease, compared with the original clothmarked surface. Except that the coarsest clothmarking gives the largest

TABLE 7

Rubber	Threads per inch in cloth used	Hardness number (1-inch ball)		
		(a)	(b)	(c)
1	15 × 15	31.5	29.5	27
6	21 × 19	25	25.5	24.5
2	33 × 32	32.5	33.5	30
5	44 × 42	30.5	31.5	29
4	44 × 44	29	30	27.5
3	64 × 44	28	30.5	26

decrease, there is no obvious relationship between the coarseness and the magnitude of the decrease.

The difference between tests (b) and (c) suggested that the buffing, presumably due to the heat generated, produced some change from which the rubber recovered only very slowly. Accordingly, a sample of No. 6 was buffed and tested at various intervals thereafter. All the tests were made at 59° F (see Table 8).

TABLE 8

Time after buffing	Hardness number (Plastometer, 1-inch ball)
10 minutes	28.7
20 minutes	26.1
55 minutes	26.0
90 minutes	25.9
120 minutes	25.6
21 hours	26.7
25 hours	26.6
44 hours	25.9
69 hours	25.8
215 hours	25.9

According to these results the rubber settles down very quickly after buffing, certainly within an hour. The cause of the difference between (b) and (c) in Table 7 therefore still remains obscure.

*Series B.*—To avoid difficulties introduced by buffing off clothmarks, a sheet of rubber was vulcanized in a mold with different portions of its surface covered by pieces of various fabrics. After stripping off the fabrics, hardness tests were made on each part with both the Pusey-Jones Plastometer and the R.A.B.R.M. gauge (Table 9).

TABLE 9  
HARDNESS NUMBER (1-INCH BALL)

Fabric (threads per inch)	Plastometer	Plastometer corrected	R.A.B.R.M. gauge
(No fabric)	63.5	70.5	70
66 × 44	65.5	72.5	80.5
60 × 40 (twill)	61.5	68.5	76.5
26 warp × 12 weft (cord tire fabric)	73.5	82	92.5

As the plastometer measured the difference between indentations under 85 grams and 1085 grams, whereas the R.A.B.R.M. gauge, as used in these tests, measured the indentation under 1000 grams, the readings for the former have been corrected to give the indentation under 1000 grams by using the known relationship between load and indentation<sup>1</sup>.



On all the clothmarked surfaces the R.A.B.R.M. gauge gives markedly higher readings than the plastometer (corrected). This may be explained as follows. The R.A.B.R.M. gauge measures the indentation relative to the plane of the foot of the gauge, which, in tests on clothmarked surfaces, corresponds approximately to the tops of the ridges, since the foot exerts only a small pressure per unit area. In the plastometer the zero is the position of the ball under an 85-gram load, which is doubtless sufficient on the small contact surface presented by a  $\frac{1}{4}$ -inch diameter sphere, to flatten out the ridges, thus giving a zero setting at a lower level than with the R.A.B.R.M. gauge. The position of the ball under the 1-kg. load is the same in both instruments, so the plastometer would give the smaller reading.

It is noteworthy that only the cord tire fabric, which gives a much rougher surface than any normal clothmarking, noticeably affects the reading of the plastometer, and the same would presumably be true of any instrument using a zero load as now specified in B.S. 903-1940.

#### TESTS OF THIN RUBBER SHEETS

A few experiments made in the course of other work, and described below, showed that the effect of lubricating a thin sheet with castor oil was much greater than the effect observed in the tests described above. Further experiments were accordingly made on thin sheets to see whether this observation was confirmed and to examine the effect of varying the thickness.

#### *Effect of French chalk and castor oil*

Tests were made on a sheet 0.57 mm. thick (see Table 10).

TABLE 10

1. Untreated.
2. Both surfaces dusted with French chalk.
3. Both surfaces lubricated with castor oil.

Ball (diameter)	Load (grams)	Hardness number			Increase with castor oil (%)
		1	2	3	
$\frac{1}{4}$ inch	200	14.3	15.5	20.3	42
$\frac{1}{4}$ inch	500	21.4	22.4	31.3	46
$\frac{1}{4}$ inch	200	20.8	22.5	28.5	37
$\frac{1}{8}$ inch	500	30.9	32.5	44.7	45

The effect of castor oil is here very large. That this effect is due to a change in the coefficient of friction between the rubber and the surfaces in contact with it was demonstrated by marking the under surface of the rubber with a network of lines and carrying out the hardness test on a glass plate through which this surface could be observed. When no lubricant was used the rubber did not slip over the glass surface when a 1-kg. load was applied to the ball. When castor oil was applied as a lubricant, however, the rubber under the ball was seen to spread out considerably when the load was applied, the reduced coefficient of friction enabling it to slip freely over the glass.

#### *Effect of French chalk, castor oil, and roughening of the surface.*

Tests were made on a variety of thin rubber sheets (see Table 11).

The effect of French chalk applied to one surface is again relatively small, i.e., about the same order as in the tests on thicker samples. Lubricating both surfaces has a somewhat greater effect, as would be expected.

TABLE 11  
HARDNESS NUMBER ( $\frac{1}{4}$ -INCH BALL)

1. Untreated.
2. Top surface lubricated with French chalk.
3. Top surface lubricated with castor oil.
4. Bottom surface lubricated with French chalk.
5. Bottom surface lubricated with castor oil.
6. Both surfaces lubricated with French chalk.
7. Both surfaces lubricated with castor oil.
8. Top surface roughened with emery paper.

Rubber	Thickness (mm.)	1	2	3	4	5	6	7	8
a	2.85	23.5	23.5	24.5	25.5	25.5	—	—	25.5
b	1.2	37	37	46.5	41.5	46	42	48.5	39.5
c	1.4	47	46.5	52.5	49	54.5	51	60	50
d	3.05	47	47.5	48	47.5	49	—	—	48
e	1.65	47.5	46	50.5	47	47.5	—	—	48
f	1.6	50	54	54.5	49	53	—	—	49
g	1.95	74.5	74.5	92.5	81	89.5	83.5	102	76
h	2.6	100.5	101	110	101	116	106.5	122	103

Castor oil has in some cases a much larger effect than in the tests on thicker samples, though the effect is not always greatest on the thinnest sheets. As the degree of compression of the rubber between the ball and the supporting surface, and hence the tendency to spread laterally, depends on the ratio of indentation to thickness, it might be expected that the effect of lubrication would be greater the larger this ratio. The figures in Table 12 provide some

TABLE 12  
PERCENTAGE INCREASE IN HARDNESS NUMBER DUE TO LUBRICATION WITH  
CASTOR OIL

Rubber	Ratio of indentation to thickness	Increase with oil on		
		Top	Bottom	Both
a	0.086	4	8	—
d	0.157	2	4	—
e	0.29	6	0	—
f	0.33	9	6	-1
b	0.36	26	24	31
c	0.37	12	16	28
h	0.42	10	16	22
g	0.44	24	20	37

evidence in support of this (the indentation is taken as the mean of the results of tests 1, 3, and 5).

Roughening the surface produces a small increase, which is of the same order as that observed in tests on thicker samples, and again shows no tendency to vary with the hardness of the rubber (see Table 13).

#### *Effect of varying thickness of rubber*

As the previous experiments had shown that the effect of lubrication, with castor oil at any rate, was greater on thin than on thick sheets, other things being equal, tests were made on various thicknesses of the same rubber. For this purpose several discs were cut from a sheet 0.73 mm. thick and tests made on various numbers of these piled to give different thicknesses. The same disc was on top in every case (see Table 14).

TABLE 13  
INCREASE IN HARDNESS NUMBER DUE TO ROUGHENING

Rubber	Increase
a	2.0
b	2.5
c	3.0
d	1.0
e	0.5
f	-1.0
g	1.5
h	2.5
Mean	1.5

TABLE 14

1. Untreated.
2. Top surface dusted with French chalk.
3. Top surface lubricated with castor oil.

No. of discs	Thickness (mm.)	Hardness number					
		$\frac{1}{4}$ -inch ball			$\frac{1}{8}$ -inch ball		
		1	2	3	1	2	3
1	0.73	35	36	41.5	48	49	54
2	1.44	52	51.5	57.5	71.5	72	78
3	2.17	60.5	63	68	87	87	93
6	4.39	80	79.5	86	110	109	117
9	6.62	91	89	94	122	123	127

French chalk has, on the whole, even less effect than in the previous experiments, the average increase being only 0.5 per cent. This may be due to the fact that the sheet had been dusted with French chalk before vulcanization, and therefore had a smooth and rather slippery surface.

The percentage increase produced by lubricating with castor oil (see Table 15) is greater the thinner the rubber as was anticipated. It is also rather

TABLE 15  
PERCENTAGE INCREASE IN HARDNESS NUMBER DUE TO LUBRICATION WITH CASTOR OIL

Thickness (mm.)	$\frac{1}{4}$ -inch ball	$\frac{1}{8}$ -inch ball
0.73	19	13
1.44	11	9.5
2.17	12	7
4.39	7.5	6.5
6.62	3	4

greater with the  $\frac{1}{4}$ -inch than with the  $\frac{1}{8}$ -inch ball, as was found in the earlier experiments (Table 10).

### SUMMARY AND CONCLUSIONS

1. Experiments have been carried out to determine how the condition of the rubber surfaces affects the results of indentation hardness tests. The following factors were investigated: the presence of French chalk and of paraffin wax bloom, lubrication with castor oil, roughening with emery paper, and clothmarking.

2. French chalk produces not more than a slight increase in the hardness number (measured depth of indentation), this being usually of the order of 1 to 3 per cent.

3. Paraffin wax bloom appears to reduce the hardness number slightly, the effect again being very small (4 per cent at most).

4. Castor oil produces a larger increase in the hardness number than does French chalk. On a given rubber the increase is greater, the smaller the thickness tested, so that on very thin sheets it may be nearly 50 per cent. There is evidence that the increase is greater for the  $\frac{1}{4}$ -inch than for the  $\frac{1}{8}$ -inch ball, and that it increases with the ratio of depth of indentation to thickness of rubber.

5. Roughening the surface with emery paper produces a small approximately constant increase (about 2 units), which can be explained by the change in the texture of the surface.

6. The effects of French chalk and castor oil agree with the theoretical deduction that reducing the coefficient of friction between the rubber and the ball and(or) supporting surface increases the indentation.

7. None of the above-mentioned treatments markedly affects the consistency of the readings.

8. The results show that for most practical purposes the results of hardness tests by the ball indentation method may be regarded as unaffected by the following variations in the condition of the rubber surface: presence or absence of French chalk or wax bloom, or variations in degree of smoothness (excluding really rough surfaces such as are produced by clothmarking).

9. Clothmarking on the rubber surface increases the hardness number obtained when no zero load is used, as in the test with a  $\frac{1}{4}$ -inch or  $\frac{1}{8}$ -inch ball and 1-kg. load, but when a zero load is used, as in the Pusey-Jones plastometer, the hardness number reading is scarcely affected except by the coarsest markings.

10. If clothmarks are removed by buffing, it is advisable to leave the rubber for some considerable time before making hardness tests, as there is evidence that buffing may produce changes that are only slowly eliminated, although this is not always the case.

#### REFERENCE

- <sup>1</sup> Scott, *J. Rubber Research* 12, 117 (1943); *RUBBER CHEM. TECH.* 17, 494 (1944).

# THE EFFECT OF AIR CIRCULATION BY CONVECTION IN THE TEST-TUBE METHOD OF HIGH- TEMPERATURE AGING OF SYNTHETIC RUBBERS \*

A. E. JUVE, H. BOXSER, D. H. REAHARD, JR., S. R. DONER,  
J. F. McWHORTER, C. G. CASHION, G. D. MCCARTHY,  
AND R. M. HOWLETT

The Tentative Method for Heat Aging of Vulcanized Natural or Synthetic Rubber by Test Tube Method<sup>1</sup>, which was developed as the result of earlier work done by this committee<sup>2</sup>, gives appreciably more reproducible results than the conventional air-oven test when the exposure temperature is in the range of 250 to 300° F. However, the degree of deterioration for equal times of exposure is less by this method than by the oven method.

In commenting on the method, A. T. McPherson, of the National Bureau of Standards, suggested that the test could be improved by providing controlled circulation of air by convection along the lines of a method which had been previously reported<sup>3</sup>.

This report gives the results of a testing program carried out to evaluate this suggestion.

## PROCEDURE

The tests reported herein were run in six coöperating laboratories. The compounds used are given below and are identical in composition with compounds A and B used in the previous study<sup>2</sup>.

	Compound A*	Compound B*
Hycar OR-15	50	50
Perbunan-26	50	50
Stearic acid	0.5	0.5
Age Rite Resin D	5	5
Zinc oxide No. 72	5	5
SRF Black (Gastex)	70	70
Sulfur		
Tuads	3	3
Captax	1.5	1.5
Plasticizer SC	15	
	<hr/> 200	<hr/> 185

\* Cured 25 minutes at 307° F.

One laboratory did the mixing, curing, and dieing-out of the test-specimens so as to reduce to a minimum possible errors from these sources.

\* Reprinted from the *ASTM Bulletin*, No. 147, pages 51-53, August 1947. The authors constitute a subsection of Section IV on Classification and Specifications of Rubber Compounds of Technical Committee D-11 on Rubber and Rubberlike Materials. This paper is a progress report. The addresses of the authors are: A. E. Juve, The B. F. Goodrich Co., Akron, Ohio; H. Boxser, Acadia Synthetic Division, Western Felt Works, Chicago, Illinois; D. H. Reahard, Jr., Enjay Co., Inc., New York, N. Y.; S. R. Doner, Manhattan Rubber Division, Raybestos-Manhattan, Inc., Passaic, New Jersey; J. F. McWhorter, Ohio Rubber Co., Willoughby, Ohio; C. G. Cashion, Firestone Tire and Rubber Co., Akron, Ohio; G. D. McCarthy, Chrysler Corporation, Detroit, Michigan; R. M. Howlett, Standard Oil Development Co., New York, N. Y.





The results of the cross-testing program are given in Tables I to V, inclusive. Tables I and II give the average test results obtained by each laboratory and the standard deviations for the nine individual specimens tested.

Tables III, IV, and V give the combined results for all laboratories. In Tables III and IV the results for the "no circulation" tests for laboratory B were omitted, since investigation of the high values for tension and elongation reported by this laboratory showed that rubber stoppers had been used instead of the cork stoppers prescribed by method D-865.

Additional work in one of the laboratories showed that in the "no circulation" method, the permeability of the stopper has a marked effect on the severity of the test. Tests using cork, cork wrapped with lead foil, cork coated with Butyl rubber, and rubber stoppers showed that as the gas permeability of the stoppers is decreased the severity of the aging (based on change in elongation) is decreased.

The results from laboratory D shown in Tables I and II are so markedly different from those obtained by the other laboratories, for both the circulating and noncirculating tests, that there is some reason to suspect that the test procedure used must have differed in some respect from that prescribed. However, these results have not been omitted from subsequent calculations.

The data shown in Tables III, IV, and V showed that the variations in chimney height over the range tested had no measurable effect on the results obtained, that the degree of deterioration (based on elongation loss) with circulation was greater than that found in the noncirculating tests, and that the

TABLE I  
VARIATION OF TESTING RESULTS BY LABORATORY FOR COMPOUND A

Testing laboratory	Height of vent tube (ft.)	Number of tests	Average tensile strength (lbs. per sq. in.)	Standard deviation, $\sigma$ , in tensile strength (lbs. per sq. in.)	Average elongation (per cent)	Standard deviation, $\sigma$ , in elongation (per cent)
A	2	9	1025.6	55.6	100	8.16
	1	9	1036.7	103.4	101.1	2.78
	$\frac{1}{2}$	9	947.8	115.0	95.6	8.32
	Control	9	1080	103.1	160	38.3
B	2	9	1362	102.6	127	8.16
	1	9	1227	145.8	123	11.05
	$\frac{1}{2}$	9	1298	346.6	127	12.7
	Control *	9	1723	102.5	287	16.3
C	2	9	1125	118.3	101	9.94
	1	9	1095	115.8	105	8.65
	$\frac{1}{2}$	9	1032	103	98	10.3
	Control	9	..	..	..	..
D	2	9	947	63.4	72.2	4.16
	1	9	930	72.1	70.0	4.72
	$\frac{1}{2}$	9	843	64.4	58.9	3.15
	Control	9	888	45.2	53.0	4.72
E	2	9	1030	170.8	108	30.4
	1	9	1105	190.3	109	28.5
	$\frac{1}{2}$	9	1073	161.3	112	24.84
	Control	9	1240	392	192	79.6
F	2	9	1003	113.9	93	6.45
	1	9	908	122.5	91	6.13
	$\frac{1}{2}$	9	938	84.6	90	5.4
	Control	9	978	119.7	129	32.9

\* Rubber stoppers used.

TABLE II  
VARIATION OF TESTING RESULTS BY LABORATORY FOR COMPOUND B

Testing laboratory	Height of vent tube (ft.)	Number of tests	Average tensile strength (lbs. per sq. in.)	Standard deviation, $\sigma$ , in tensile strength (lbs. per sq. in.)	Average elongation (per cent)	Standard deviation in elongation (per cent)
A	2	9	1164	55.5	80	6.66
	1	9	1167	77.1	77.8	7.85
	$\frac{1}{2}$	9	1142	55.5	77.8	7.85
	Control	9	1294	254.7	134	45.1
B	2	9	1244	91.2	79	12.4
	1	9	1103	148.4	64	12.4
	$\frac{1}{2}$	9	1214	55.8	83	6.1
	Control*	9	2137	178.4	234	26.8
C	2	9	1201	89.5	83	3.65
	1	9	1252	87.4	83	11.50
	$\frac{1}{2}$	9	1176	42.6	84	6.88
	Control	9	..	..	..	..
D	2	9	964	21.2	52.2	4.15
	1	9	1062	48.3	56.7	4.72
	$\frac{1}{2}$	9	1047	52.1	55.6	4.94
	Control	9	979	37	53	4.72
E	2	9	1230	40.4	88	20.4
	1	9	1198	96.3	85	16.4
	$\frac{1}{2}$	9	1170	170.9	81	20.2
	Control	9	1116	340	110	51.9
F	2	9	1073	106.2	79	5.63
	1	9	1020	79.9	79	5.66
	$\frac{1}{2}$	9	1107	100.4	83	5.66
	Control	9	988	47	94	6.47

\* Rubber stoppers used.

TABLE III  
COMBINED DATA—COMPOUND A

Height vent tube (ft.)	Average tensile strength (lbs. per sq. in.)	Standard deviation in tensile strength (lbs. per sq. in.)	Average elongation (per cent)	Standard deviation in elongation (per cent)	Number of tests
2	1082	176.8	100	21.7	54
1	1050	168.9	100*	21.6*	54
$\frac{1}{2}$	1022	183.1	97	24.5	54
No circulation	1046 (960)†	246.2 (268)	134 (79.0)	69.8 (34.2)	36 (42)
Not aged	1930 (1818)	76.6 (92)	647 (851)	39.9 (29.6)	15 (12)

\* 53 tests were reported.

† Values in parentheses from data previously obtained.

TABLE IV  
COMBINED DATA—COMPOUND B

Height vent tube (ft.)	Average tensile strength (lbs. per sq. in.)	Standard deviation in tensile strength (lbs. per sq. in.)	Average elongation (per cent)	Standard deviation in elongation (per cent)	Number of tests
2	1146	132.3	77	16.3	54
1	1134	124.9	74	15	54
$\frac{1}{2}$	1143	106.1	77	14.2	54
No circulation	1094 (1233)*	250.7 (277)	98 (88)	45.5 (48.7)	36 (42)
Not aged	2286 (2099)	178 (818)	536 (646)	24.3 (27.5)	15 (12)

\* Values in parentheses from data previously obtained.

TABLE V  
PERCENTAGE LOSS IN WEIGHT OF AGED SAMPLES FOR  
COMPOUND A AND COMPOUND B

Compound	Number of tests	Vent tube height (ft.)	Average loss of weight (per cent)	Standard deviation, $\sigma$ (per cent)
A	27	2	1.36	0.30
	27	1	1.40	0.42
	27	$\frac{1}{2}$	1.21	0.33
	27	No circulation	1.07	0.38
B	27	2	0.85	0.28
	27	1	0.84	0.21
	27	$\frac{1}{2}$	0.67	0.24
	27	No circulation	0.41	0.19

reproducibility of the test was appreciably improved by introducing circulation by convection. The heat-loss results were somewhat scattered and show no well-defined relation to the velocity of air circulation. However, the losses in the circulating-air tests were generally higher than those in the noncirculating tests. Compound A, which contains Plasticizer SC, showed a greater loss than Compound B.

In Tables III and IV the values shown in parentheses are derived from data previously reported<sup>2</sup> and show that the reproducibility found in this test program checks fairly well with that previously found.

It was observed in the course of the circulating-air tests that considerable material was deposited on the inside of the exhaust tube. This consisted principally of colorless crystals which were identified as tetramethylthiourea and dimethylammonium dimethyldithiocarbamate.

### CONCLUSIONS AND RECOMMENDATIONS

By modifying the present test-tube method of high-temperature aging to permit air circulation by convection, the test is made appreciably more severe, but at the same time more reproducible.

The velocity of air circulation under the conditions used here, which varied over a three-fold range from 1.1 to 3.4 changes of air per hour, did not affect the results obtained.

The loss in weight during aging was somewhat greater in the circulating-air tests than in the stoppered-tube tests.

The poorer reproducibility of the stoppered test-tube method over the circulating-air method is thought to be due to variations in the permeability of the stoppers used. The more impermeable the stopper, the less severe is the test.

It is recommended that the present test-tube aging method D-865 be amended to require the use of a pair of glass tubes extending through the stopper using the dimensions and arrangement illustrated in Figure 1.

### REFERENCES

- <sup>1</sup> 1946 *Book of A.S.T.M. Standards*, Part III-B, D865-46T, p. 977.
- <sup>2</sup> McCarthy, Juve, Boxser, Sanger, Doner, Cunningham, McWhorter, and Crossley, *A. S. T. M. Bull.* No. 132, p. 33, Jan. 1945; *RUBBER CHEM. TECH.* 18, 667 (1945).
- <sup>3</sup> Holt and McPherson, *Rubber Age* (N. Y.) 36, 121 (1934).

# EFFECT OF FUNGICIDES ON NATURAL AND SYNTHETIC RUBBER\*

J. L. STIEF, JR., AND J. J. BOYLE

THE ENGINEER BOARD, CORPS OF ENGINEERS, U. S. ARMY, FORT BELVOIR, VA.

During the recent war a great part of the military operations were conducted in warm, humid, tropical regions, ideal for the growth of fungi. The protection of the cotton cloth<sup>1</sup> used in rubber-coated fabrics thus became a major problem of the armed forces. Because the area was of minor importance in the world consumer market, comparatively little work had been done on this problem by the research laboratories of private industry. A tropical testing chamber<sup>2</sup> which simulated tropical conditions was built at Fort Belvoir to study the problems of fungus growth and effective countermeasures.

The problem was complicated by the possibility that the fungicide which had a protective effect on the cloth might have had a destructive effect on the rubber coating. Tests on pentachlorophenol and 2,2'-methylene-bis (4-chlorophenol) by two industrial concerns had indicated that these two fungicides had no adverse effect on either natural rubber or GR-S when used in small concentrations. Tests by another industrial concern had indicated that salicylanilide was satisfactory for use with natural rubber and Neoprene. However, because of the meager amount of information available, a study was conducted to determine what fungicides, and in what concentrations, might abnormally deteriorate rubber coatings.

This problem was divided into two parts. The first was to determine the effect of the various fungicides on the physical properties of natural and synthetic rubber when incorporated directly into the rubber compound before vulcanizing. The second part was to determine the effect of the fungicides

TABLE I  
COMPOUNDING FORMULAS

Natural rubber (Cured 20 min. at 300° F)		GR-S (Cured 35 min. at 300° F)		Neoprene (Cured 20 min. at 300° F)	
Component	Parts by wt.	Component	Parts by wt.	Component	Parts by wt.
Smoked sheet	100.0	GR-S	100.0	Neoprene GN-A	100.0
Reogen	2.0	Stearic acid	2.0	XLC magnesia	4.0
Stearic acid	3.0	Zinc oxide	5.0	Stearic acid	0.5
Pine tar	1.0	EPC black	50.0	EPC black	30.0
Neozone D	1.0	Sulfur	2.0	Neozone D	2.0
Zinc oxide	5.0	Altax	0.75	Accelerator 552	0.1
EPC black	50.0	Barak	1.0	Zinc oxide	5.0
Sulfur	3.0	Fungicide	2.0	Fungicide	2.0
Altax	2.0				
Thionex	0.2				
Fungicide	2.0				

\* Reprinted from *Industrial and Engineering Chemistry*, Vol. 39, No. 9, pages 1136-1138, September 1947. This paper was presented before the Division of Rubber Chemistry at the 110th Meeting of the American Chemical Society, Chicago, Illinois, September 10-13, 1946.

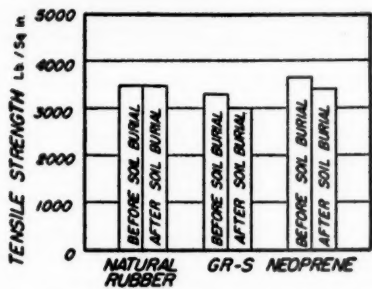


FIG. 1.—Effect of exposure to fungi on untreated rubber.

on the adhesion, abrasion, and general wearing qualities of coated fabrics when the fungicide is impregnated into the fabric prior to coating.

The work to date covers five fungicides and three types of rubber. The fungicides tested include copper naphthenate, pyridylmercuric stearate, salicylanilide, pentachlorophenol, and 2,2'-methylene-bis(4-chlorophenol), some-

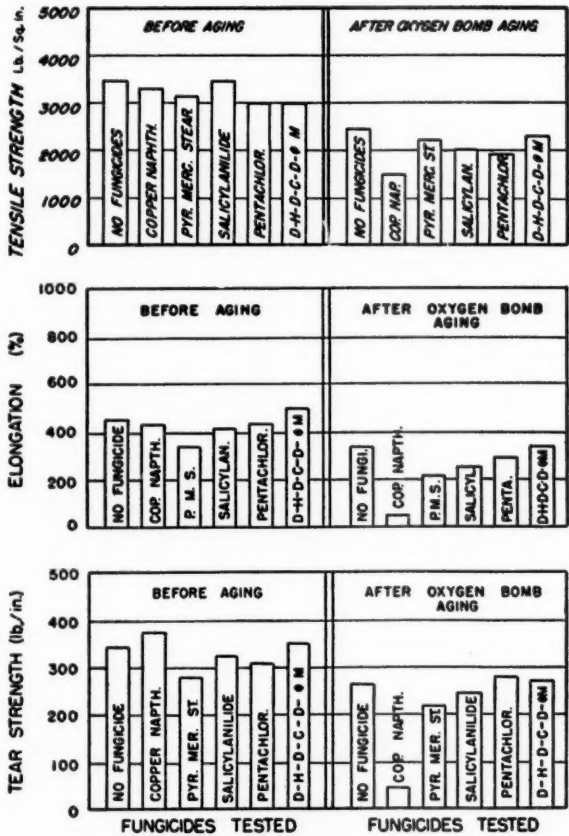


FIG. 2.—Effect of fungicides on natural rubber.

times designated as dihydroxydichlorodiphenylmethane (an abbreviated form of the latter designation is used in the figures for simplicity). These fungicides were selected as representative of the types found most effective in preventing the fungus deterioration of cotton fabrics in a considerable number of tests conducted by The Engineer Board. Table I lists the types of rubber tested and the compounding formulations used. Natural rubber, GR-S, and Neoprene are the subject of this report, but other coating materials such as vinyl

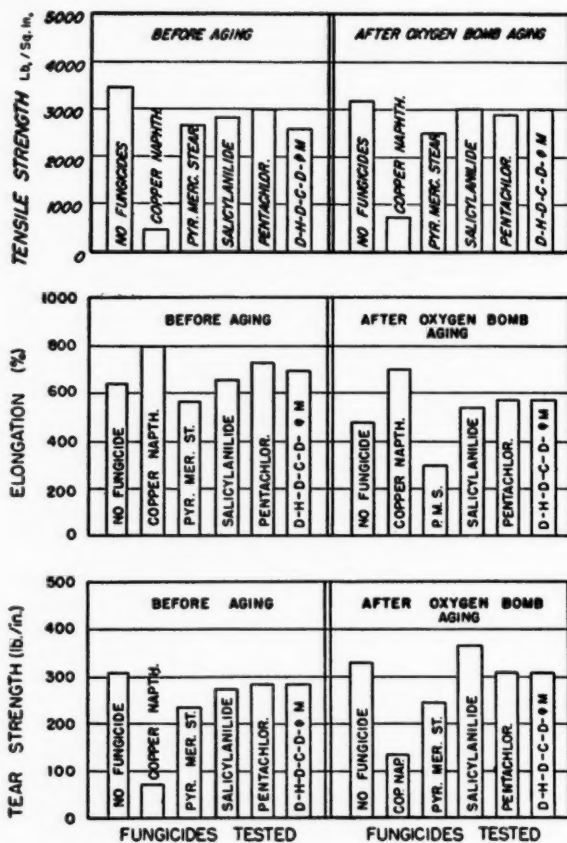


FIG. 3.—Effect of fungicides on GR-S.

butyral, vinyl copolymers, Butyl rubber, and butadiene-acrylonitrile rubber, are to be included in future work.

#### MIXING, CURING, TESTING

In general, the procedure used in preparing the test specimens was that recommended by A.S.T.M. specifications. A separate batch of rubber was milled for each fungicide, and a batch containing no fungicide was used as control. The fungicide was milled directly into the rubber, using two parts of fungicide per hundred parts of polymer. No difficulty was encountered in



form  
cides  
nting  
tests  
ested  
Neo-  
vinyl

incorporating any of these fungicides, although the concentrated copper naphthenate, a sticky gummy substance, was somewhat harder to handle than the other fungicides which were all dry powders. Slabs were press-cured in an A.S.T.M. four-cavity mold and were die cut into test specimens. These were tested for tensile strength, ultimate per cent elongation, modulus at 300 per cent elongation, Shore hardness, and tear strength. The effect of the fungicides on the weathering and age resistance of the vulcanizate was investigated

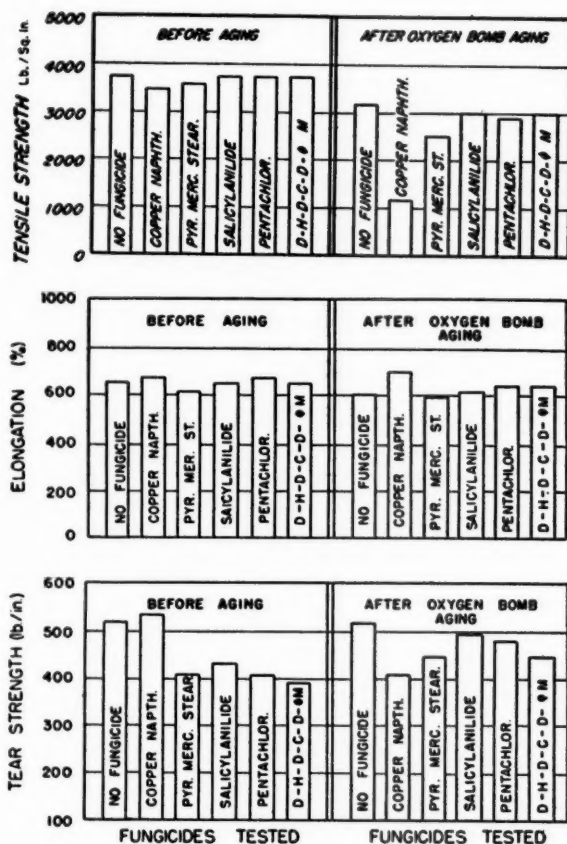


FIG. 4.—Effect of fungicides on Neoprene.

by subjecting test specimens to light aging, heat aging, oxygen bomb aging, and soil burial. However, only the tensile strength, elongation, tear strength, and unaged and oxygen bomb aging test conditions are reported here, since they are sufficient to illustrate the observed effects.

The results of the soil burial tests on vulcanizates containing no added fungicide, summarized in Figure 1, indicated that there was no significant loss of strength due to fungus attack. No visual evidence of fungus growth was observed. Therefore, it appeared that no fungicide was necessary for the protection of the vulcanizates themselves.

## EFFECT OF FUNGICIDES

The test results summarized in Figure 2 show that none of the fungicides tested had any appreciable effect on the unaged natural rubber test specimens. However, test specimens containing copper naphthenate appeared to age more rapidly in the oxygen bomb test. The rubber became much stiffer, as evidenced by the sharp decrease in elongation at break. Tear strength was considerably reduced. Thus it seemed probable that fabrics treated with copper naphthenate and having a natural rubber coating might be expected to crack when used after lengthy periods of storage. Pyridylmercuric stearate, salicylanilide, pentachlorophenol, and 2,2'-methylene-bis(4-chlorophenol) had little or no adverse effect on natural rubber.

The results on GR-S (Figure 3) indicated that copper naphthenate caused a serious loss of strength when incorporated into GR-S. Tensile and tear strengths were materially reduced, and elongation at break was increased. The copper naphthenate had a considerable retarding effect on the rate of cure of GR-S. The vulcanized slabs were soft and tacky when removed from the mold. Very little resilience, or snap, was observed. This test was made on a GR-S vulcanizate containing 2 per cent fungicide. Other tests on specimens containing 1 and 0.5 per cent fungicide indicated a considerably lesser and progressively decreasing effect. Pyridylmercuric stearate had a very slight injurious effect on GR-S. Salicylanilide, pentachlorophenol, and 2,2'-methylene-bis(4-chlorophenol) had little or no adverse effect on the physical properties of GR-S.

The results of tests on Neoprene (Figure 4) indicated that pyridylmercuric stearate, salicylanilide, pentachlorophenol, and 2,2'-methylene-bis(4-chlorophenol) caused no measurable loss of tensile strength (within the limits of experimental error), and only a very slight reduction of tear strength. Copper naphthenate caused an appreciable loss of tensile strength after aging, but apparently produced an increase in the ultimate elongation and tearing strength.

## REFERENCES

- <sup>1</sup> Greathouse and Ames, *Mycologia* **37**, No. 1, 138 (1945).
- <sup>2</sup> Cooke and Vicklund, *Ind. Eng. Chem. Anal. Ed.* **18**, 59 (1946).